

# Electronic structure

## Hartree-Fock method in molecules and solids (1)

- Hermann Haken & Hans C. Wolf, *The Physics of Atoms and Quanta*, Springer, 2004
- Hermann Haken & Hans C. Wolf, *Molecular Physics and Elements of Quantum Chemistry*, Springer, 2003
- Attila Szabo & Neil Ostlund, *Modern Quantum Chemistry*, Dover, 1996

# **Brief review of Quantum mechanics: Results of atoms**

**Electronic structure of atoms**

$$\hat{H} = \hat{T} + \hat{V} \quad \text{Typically, we prefer to discuss in position space.}$$

$$\hat{T} = \frac{1}{2m} \hat{\mathbf{p}}^2 \quad \hat{\mathbf{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z) \quad \hat{p}_j = \frac{\hbar}{i} \frac{\partial}{\partial x_j} \quad \text{Basic example of vector operator}$$

$$\hat{V} = V(\mathbf{r})$$

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \hat{H}\psi(\mathbf{r}, t)$$

In many cases, the hamiltonian does not contain time explicitly, so

$$\psi(\mathbf{r}, t) = e^{-iEt/\hbar} \psi(\mathbf{r})$$

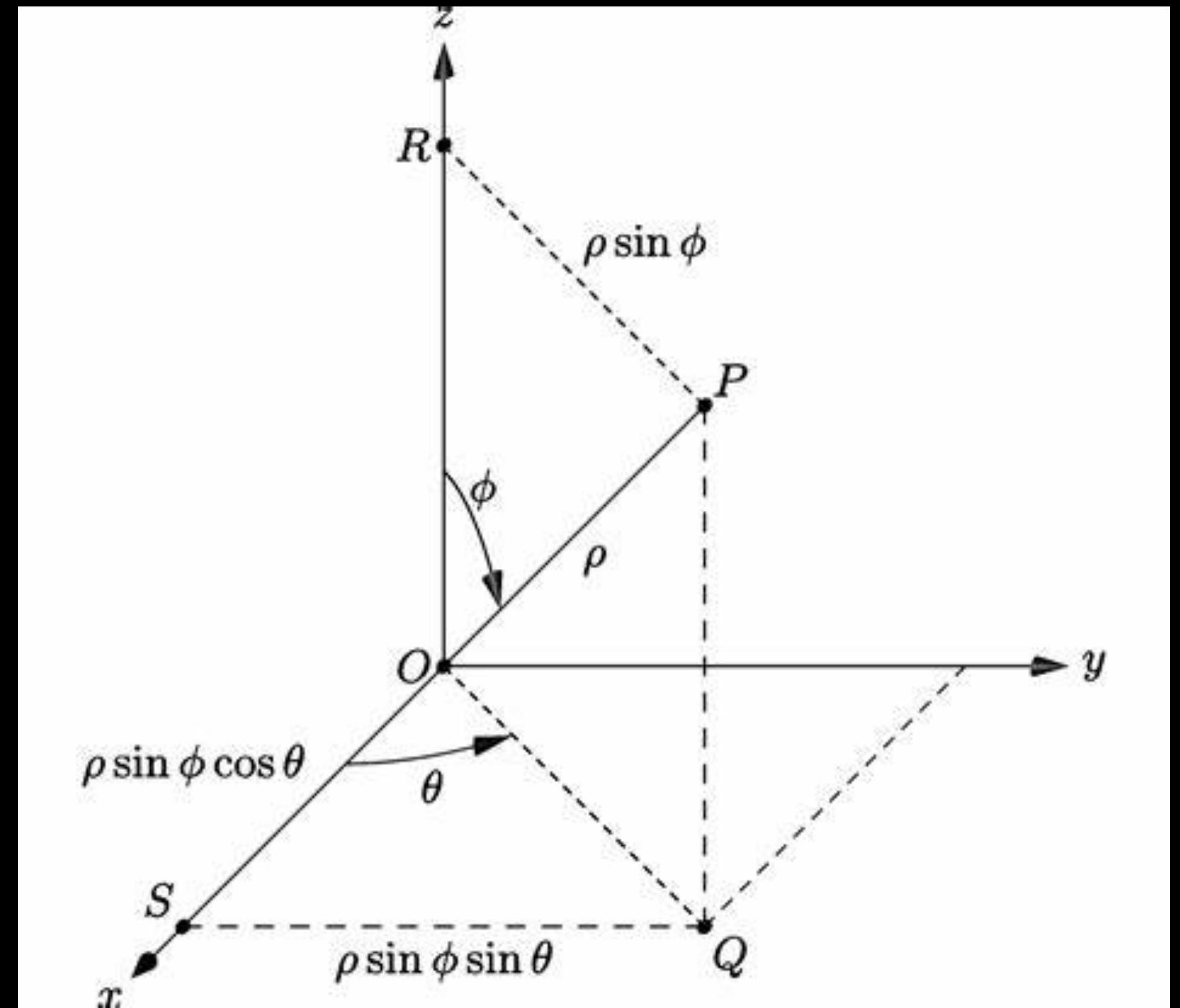
$$\boxed{\hat{H}\psi_\nu(\mathbf{r}) = E_\nu \psi_\nu(\mathbf{r})}$$

# Quantum mechanical results of H-like Atom

$$\hat{H} = -\frac{\hbar^2}{2m_0} \nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \quad \mathbf{r} = (r, \theta, \phi)$$

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)P_l^m(\cos \theta)e^{im\phi}$$

$$E_n = -\frac{m_0 Z^2 e^4}{2\hbar^2 (4\pi\epsilon_0)^2} \frac{1}{n^2} = -\frac{13.6}{n^2} \text{ eV}$$



$$F_{l,m}(\theta, \phi) \equiv P_l^m(\cos \theta) e^{im\phi}$$

$$l = 0, \quad F_{0,0} = \frac{1}{\sqrt{4\pi}}$$

$$l = 1, \quad F_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r}$$

$$l = 1, \quad F_{1,\pm 1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi} \Rightarrow \pm \sqrt{\frac{3}{8\pi}} \frac{x \pm y}{r}$$

$$Y_{l,m}(\theta, \phi)$$

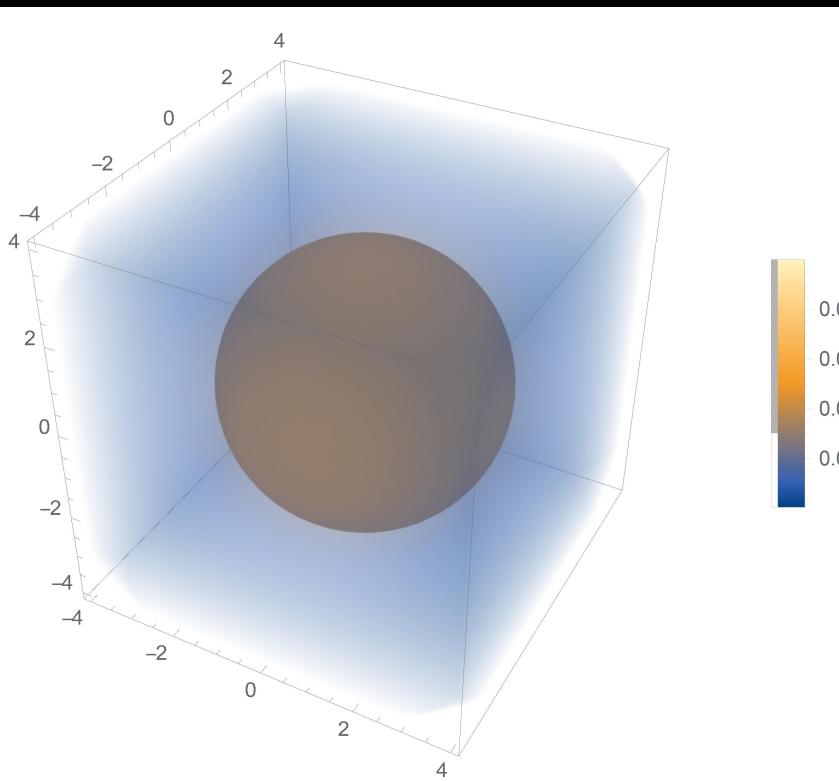
*Spherical harmonics  
S. Hassani,  
Mathematical Physics,  
2nd edition, Springer,  
2013, Chapter 13*

$$\frac{(F_{1,1} + F_{1,-1})}{2} = \sqrt{\frac{3}{8\pi}} \frac{x}{r}$$

$$\frac{(F_{1,1} - F_{1,-1})}{2i} = \sqrt{\frac{3}{8\pi}} \frac{y}{r}$$

$$F_{1,|1|}, \quad F_{1,|1|}'$$

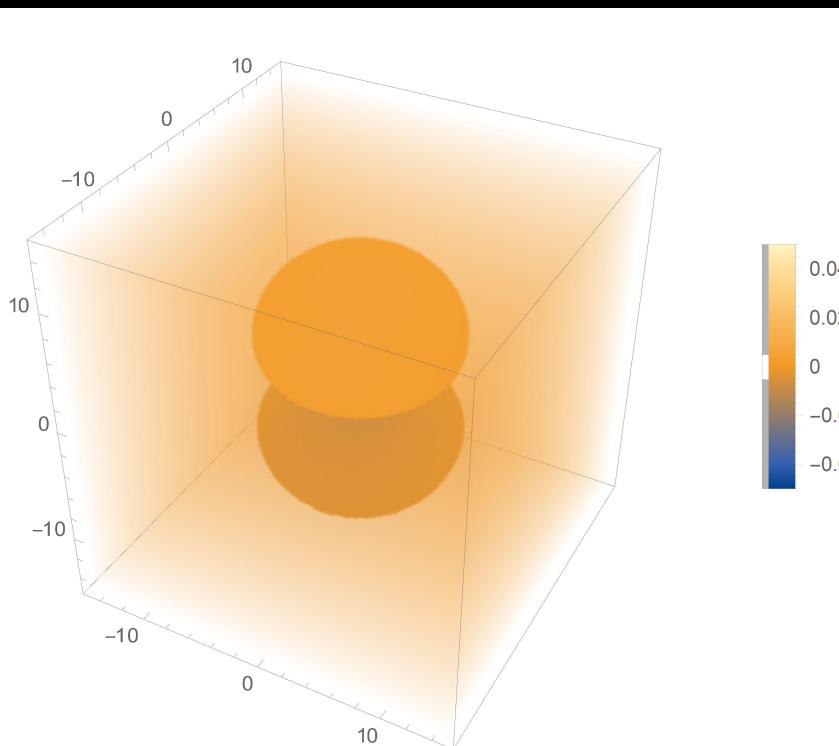
$n = 1, l = 0$



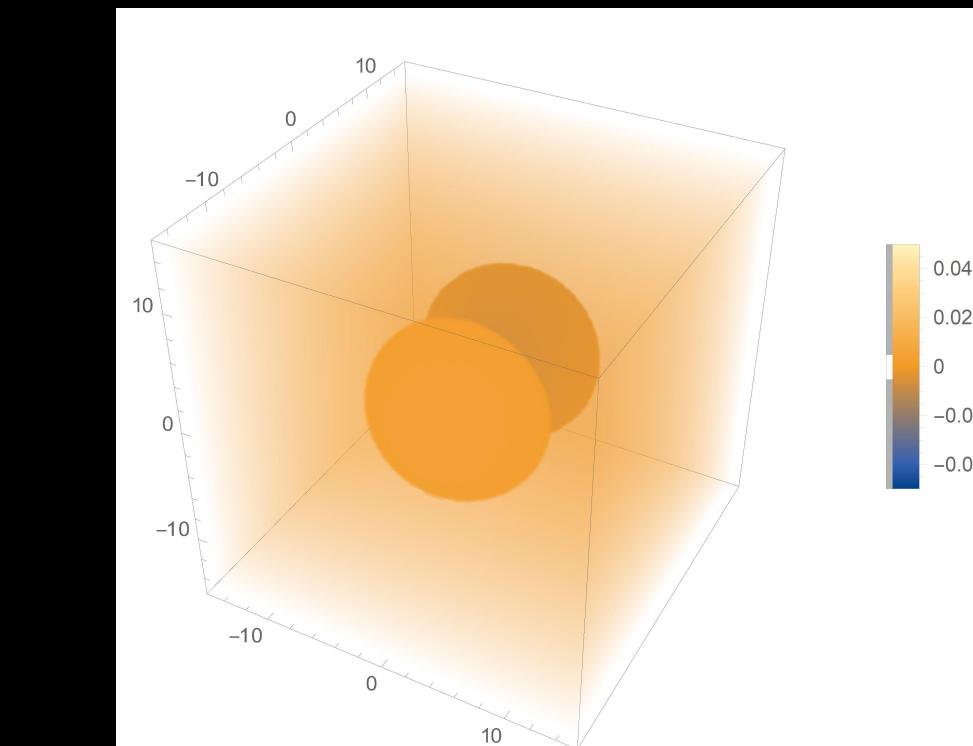
s: sharp  
p: principal  
d: diffuse  
f: fundamental

Haken & Wolf,  
*The Physics of Atoms and Quanta*,  
Springer, 2010, pp. 176

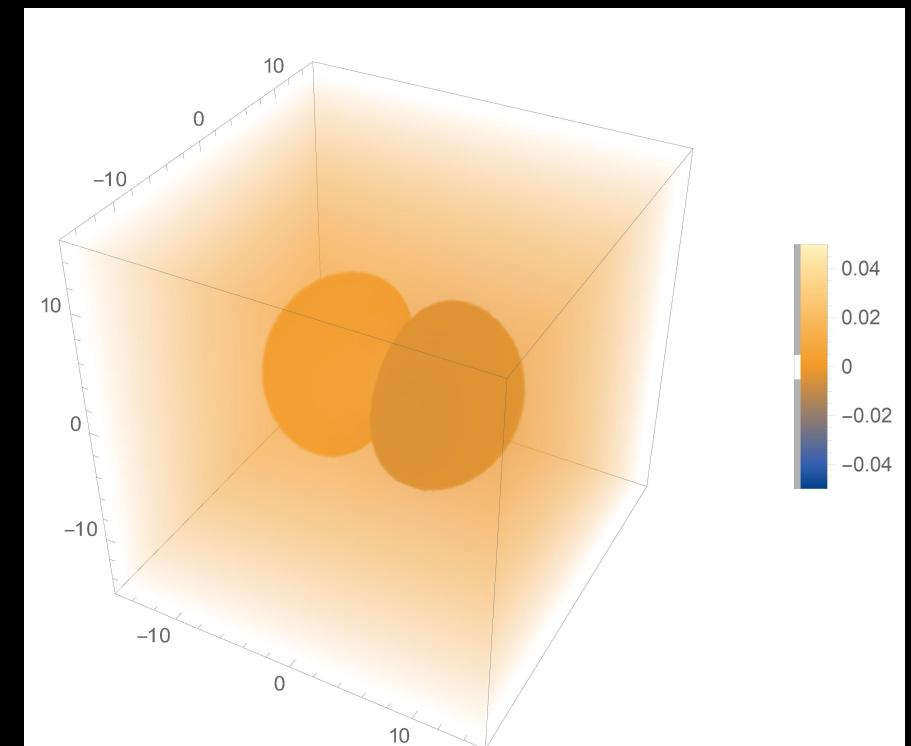
$n = 2, l = 1$



$m = 0$



$m = -1$



$m = 1$

$$R_{n,l} = N_{n,l} e^{-\kappa_n r} r^l L_{n+1}^{2l+1}(2\kappa_n r)$$

Here  $N_{n,l}$  is a normalization factor, defined as:

$$\int_0^\infty R^2 r^2 dr = 1$$

$$\kappa_n = - \frac{m_0 Ze^4}{\hbar^2(4\pi\varepsilon_0)} \frac{1}{n}$$

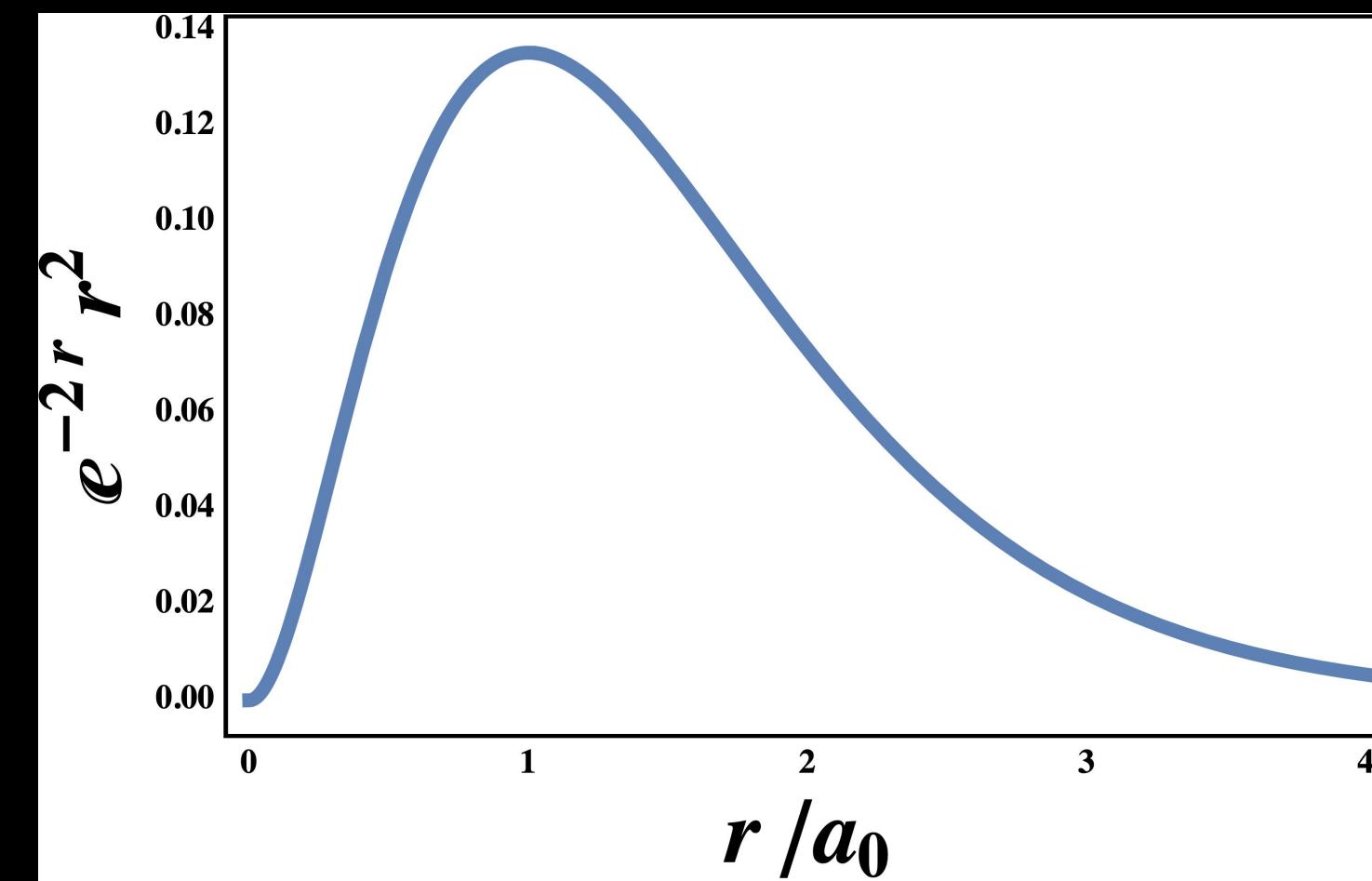
$$L_{n+1}^{2l+1}(\rho) \equiv \frac{d^{2l+1}}{d\rho^{2l+1}} L_{n+1}$$

A derivative of the *Laguerre polynomials*  $L_{n+1}$

$$L_{n+1}(\rho) = e^\rho \frac{d^{n+1} e^{-\rho} \rho^{n+1}}{d\rho^{n+1}}$$

Example:  $L_1^1 = -1$

$$R_{1,0} = Ne^{-\kappa_1 r}$$



$$R_{1,0} = Ne^{-\kappa_1 r}$$

$$r^2 |R_{1,0}|^2 = N^2 r^2 e^{-2\kappa_1 r}$$

In quantum chemistry, the first Laguerre polynomial is called *Slater Type Orbital* (STO).  
It's used in ADF (Amsterdam Density Functional).

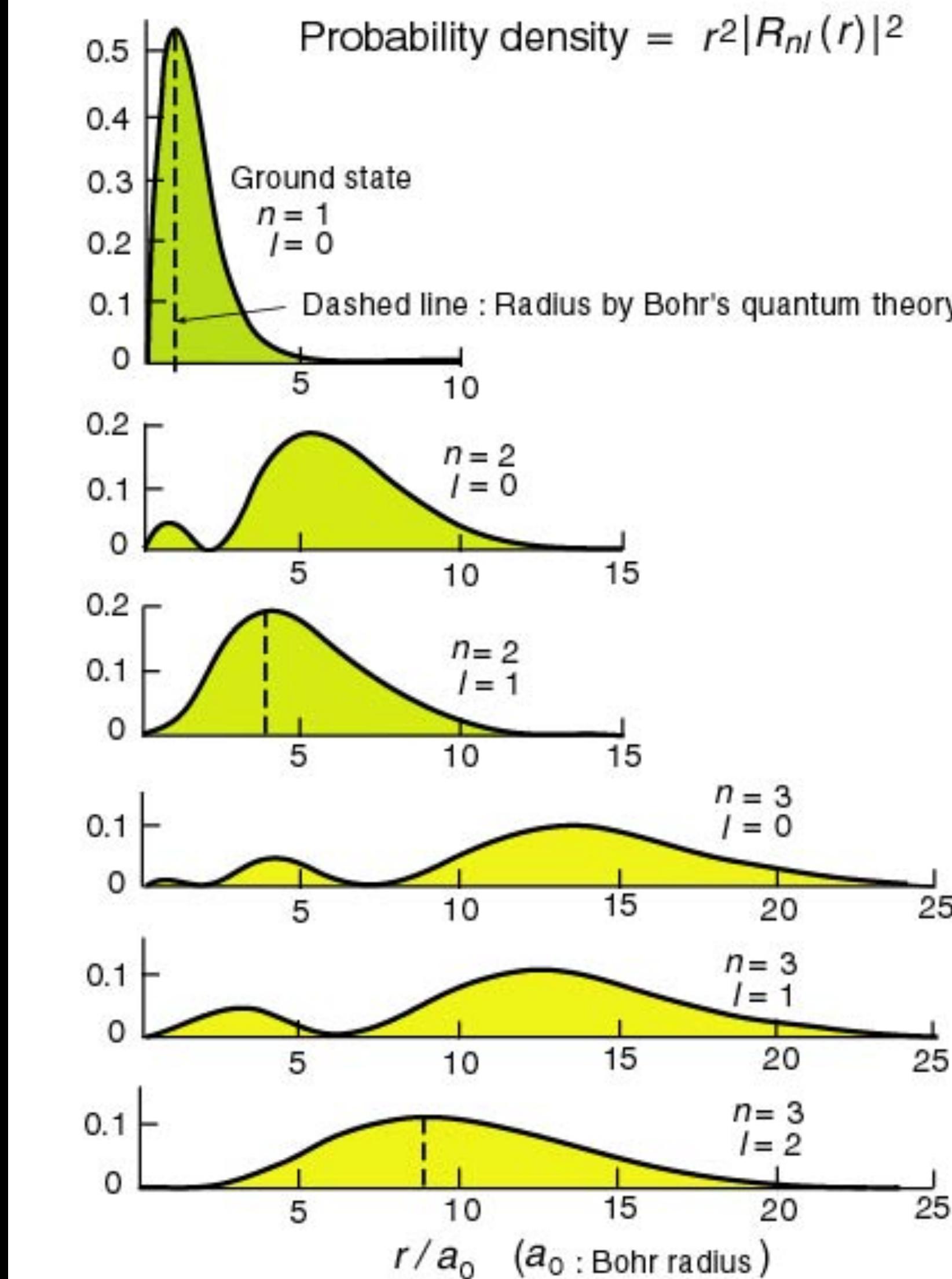
**ADF**

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Fig. (C)

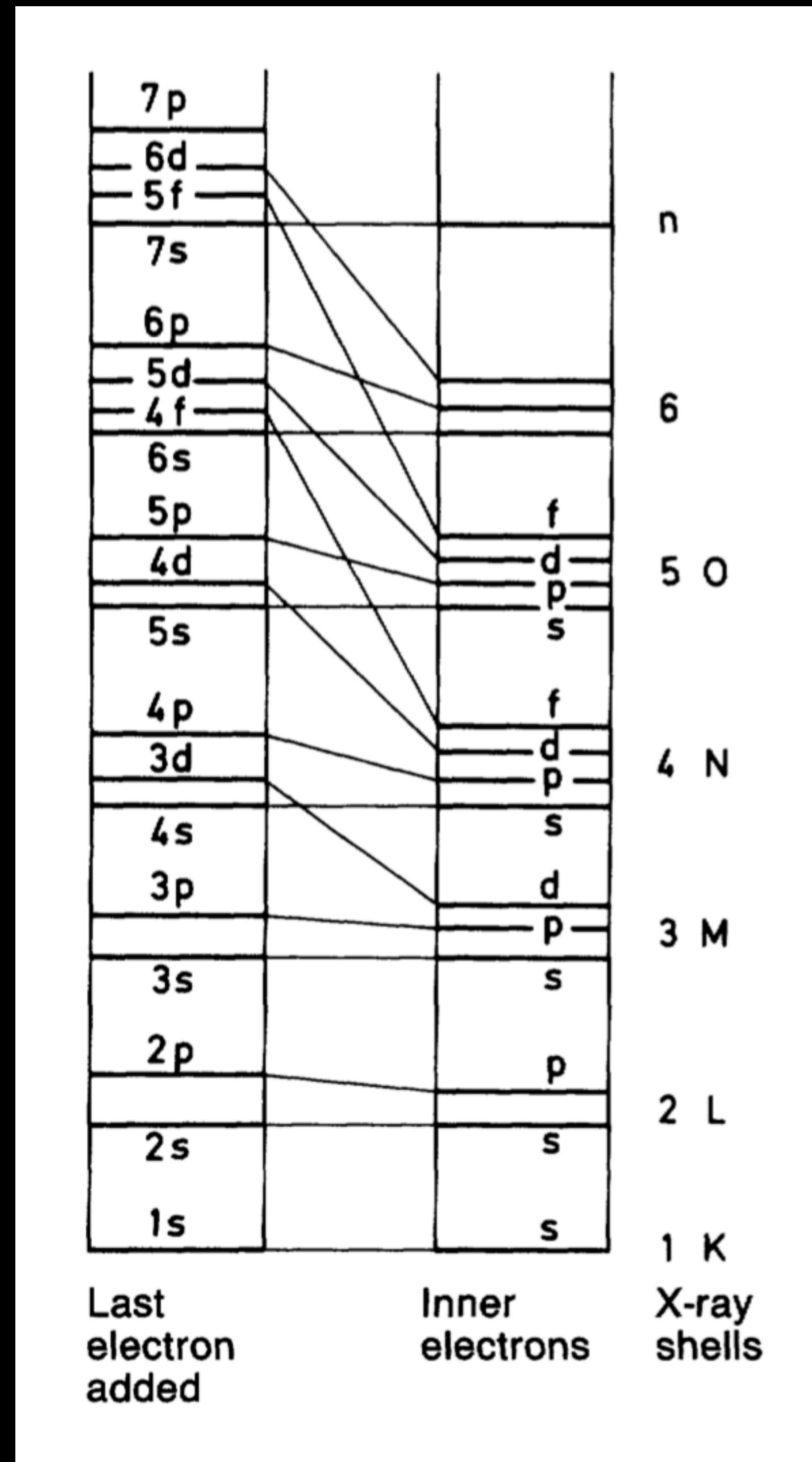


Internet Seminar  
**Microscopic World -2-**  
Introduction to Quantum Mechanics

Dr. Kenjiro Takada  
Emeritus professor of Kyushu University

[http://ne.phys.kyushu-u.ac.jp/seminar/MicroWorld2\\_E/2Part3\\_E/2P32\\_E/hydrogen\\_atom\\_E.htm](http://ne.phys.kyushu-u.ac.jp/seminar/MicroWorld2_E/2Part3_E/2P32_E/hydrogen_atom_E.htm)

<https://demonstrations.wolfram.com/HydrogenAtomRadialFunctions/>

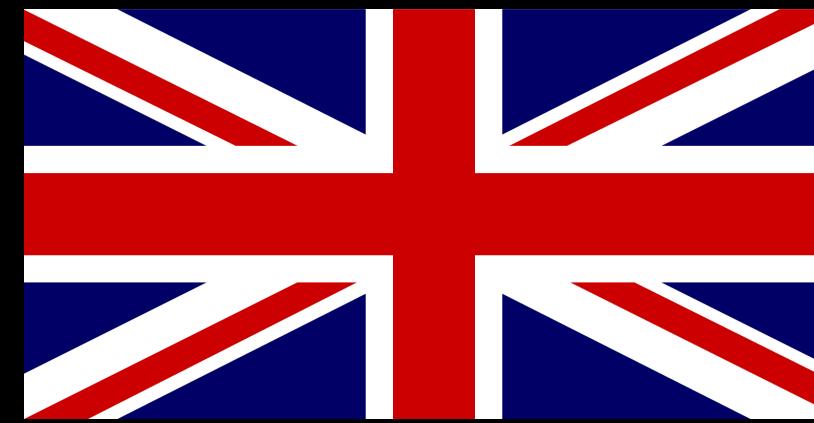


Electronic structure of many electron atoms

Hermann Haken & Hans C. Wolf, *The Physics of Atoms and Quanta*, Springer, 2004

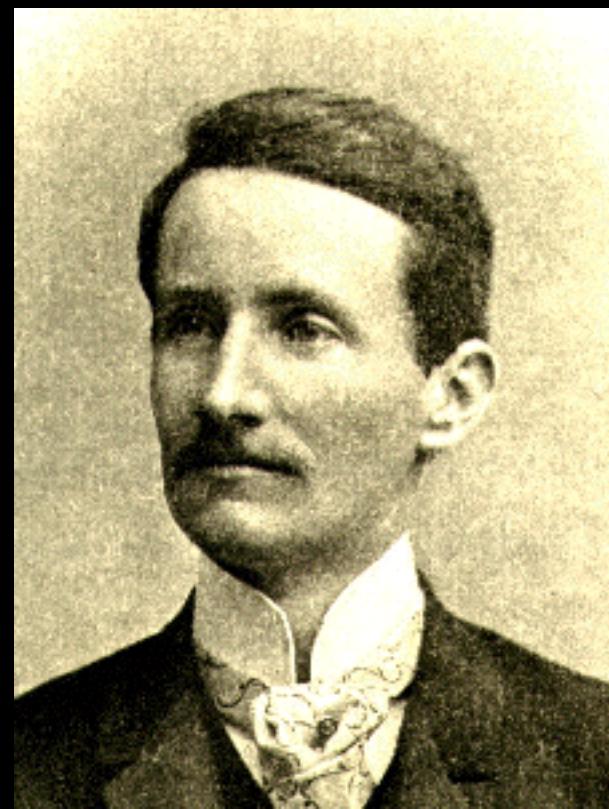
# Quantum mechanics for molecules

From brute-force to **Hartree-Fock Self-Consistent Field**



<https://mathshistory.st-andrews.ac.uk/Biographies/Hartree/>

<https://physicstoday.scitation.org/do/10.1063/pt.6.6.20171222a/full/>



Walter Ritz

Sion (Switzerland) February 22, 1878 – Göttingen July 7, 1909

# Variational method

[Published: 14 February 2018](#)

The Deep Ritz Method: A Deep Learning-Based Numerical Algorithm for Solving Variational Problems

[Weinan E & Bing Yu](#)✉

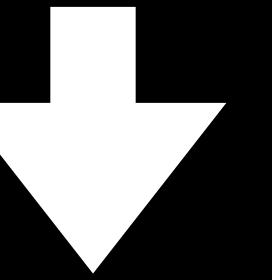
[Communications in Mathematics and Statistics](#) **6**, 1–12 (2018) | [Cite this article](#)

4247 Accesses | 119 Citations | [Metrics](#)

The variation principle:

Given a normalized wave function  $|\tilde{\Phi}\rangle$  that satisfies the appropriate boundary conditions, then the *expectation value* of the Hamiltonian is an *upper bound* to the exact ground state energy.

$$\langle \tilde{\Phi} | \tilde{\Phi} \rangle = 1$$



$$\langle \tilde{\Phi} | \hat{H} | \tilde{\Phi} \rangle \geq E_0$$

$$\text{or } \frac{\langle \tilde{\Phi} | \hat{H} | \tilde{\Phi} \rangle}{\langle \tilde{\Phi} | \tilde{\Phi} \rangle} \geq E_0$$

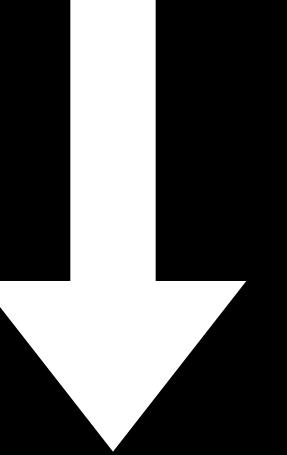
Once  $|\tilde{\Phi}\rangle = |\Phi_0\rangle$  the identity holds.

Proof of the variation principle:  
 (With the help of completeness of basis)

$$\sum_{\alpha} |\Phi_{\alpha}\rangle\langle\Phi_{\alpha}| = 1$$

$$\langle\tilde{\Phi}|\tilde{\Phi}\rangle = 1 = \sum_{\alpha\beta} \langle\tilde{\Phi}|\Phi_{\alpha}\rangle\langle\Phi_{\alpha}|\Phi_{\beta}\rangle\langle\Phi_{\beta}|\tilde{\Phi}\rangle = \sum_{\alpha} |\langle\Phi_{\alpha}|\tilde{\Phi}\rangle|^2$$

$$\langle\tilde{\Phi}|\hat{H}|\tilde{\Phi}\rangle = \sum_{\alpha} \langle\tilde{\Phi}|\Phi_{\alpha}\rangle\langle\Phi_{\alpha}|\hat{H}|\Phi_{\alpha}\rangle\langle\Phi_{\alpha}|\tilde{\Phi}\rangle = \sum_{\alpha} E_{\alpha} |\langle\Phi_{\alpha}|\tilde{\Phi}\rangle|^2$$



$$\langle\tilde{\Phi}|\hat{H}|\tilde{\Phi}\rangle \geq \sum_{\alpha} E_0 |\langle\Phi_{\alpha}|\tilde{\Phi}\rangle|^2 = E_0 \sum_{\alpha} |\langle\Phi_{\alpha}|\tilde{\Phi}\rangle|^2 = E_0$$

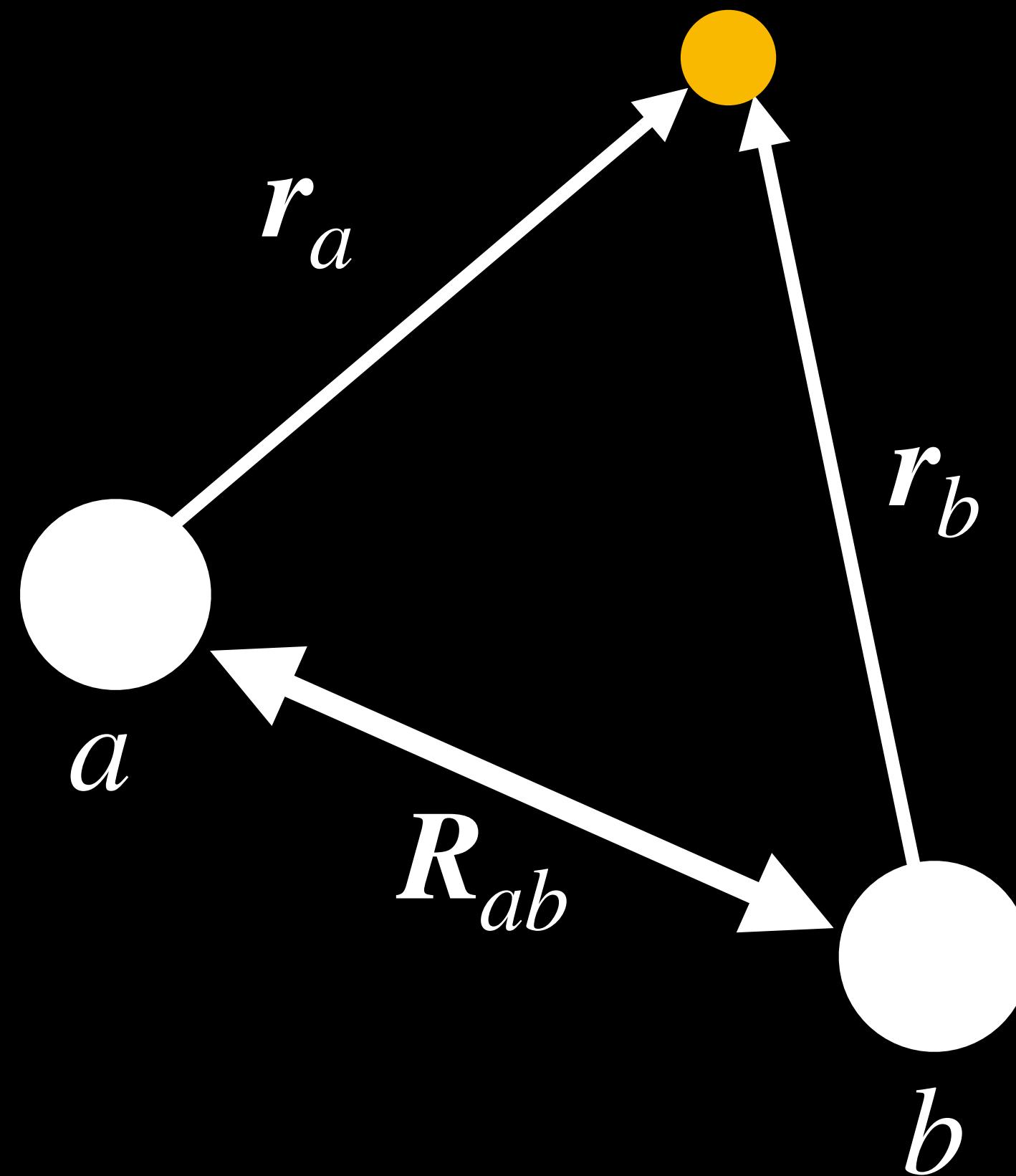


Step further: hydrogen molecular ion



# Quantum mechanical treatment of H<sub>2</sub><sup>+</sup>

## Constructive interference: bonding state

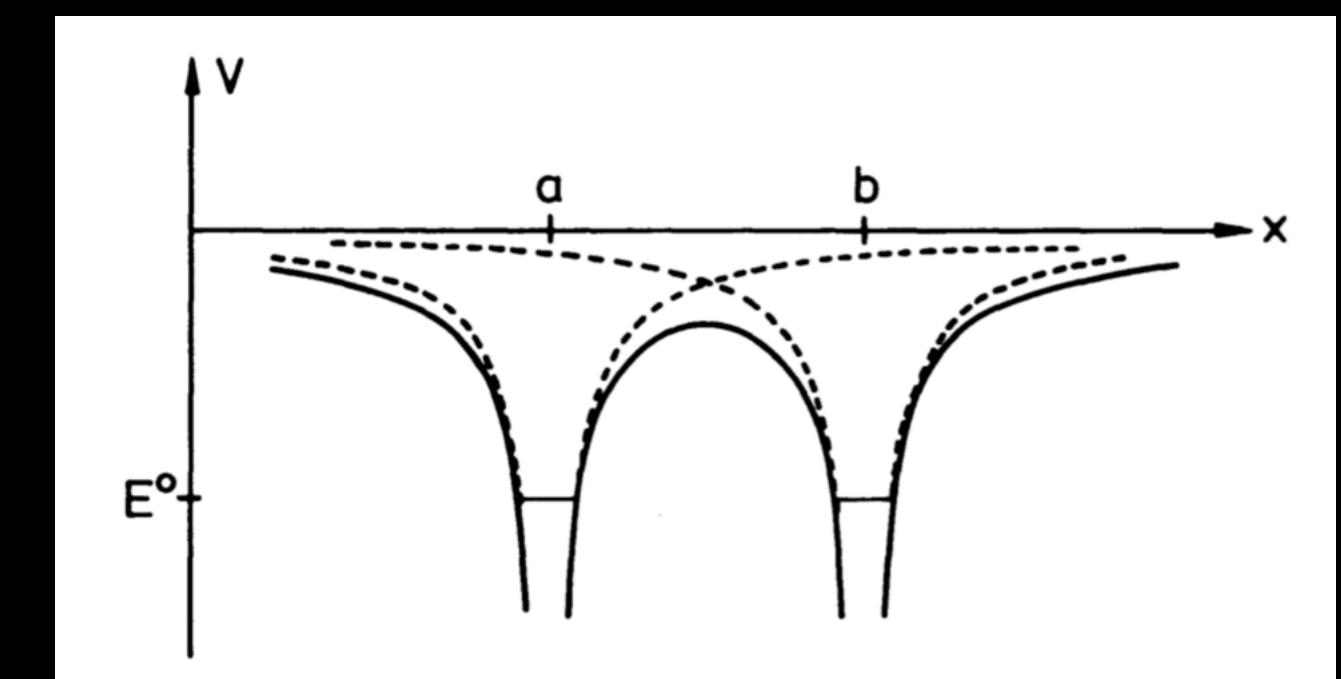


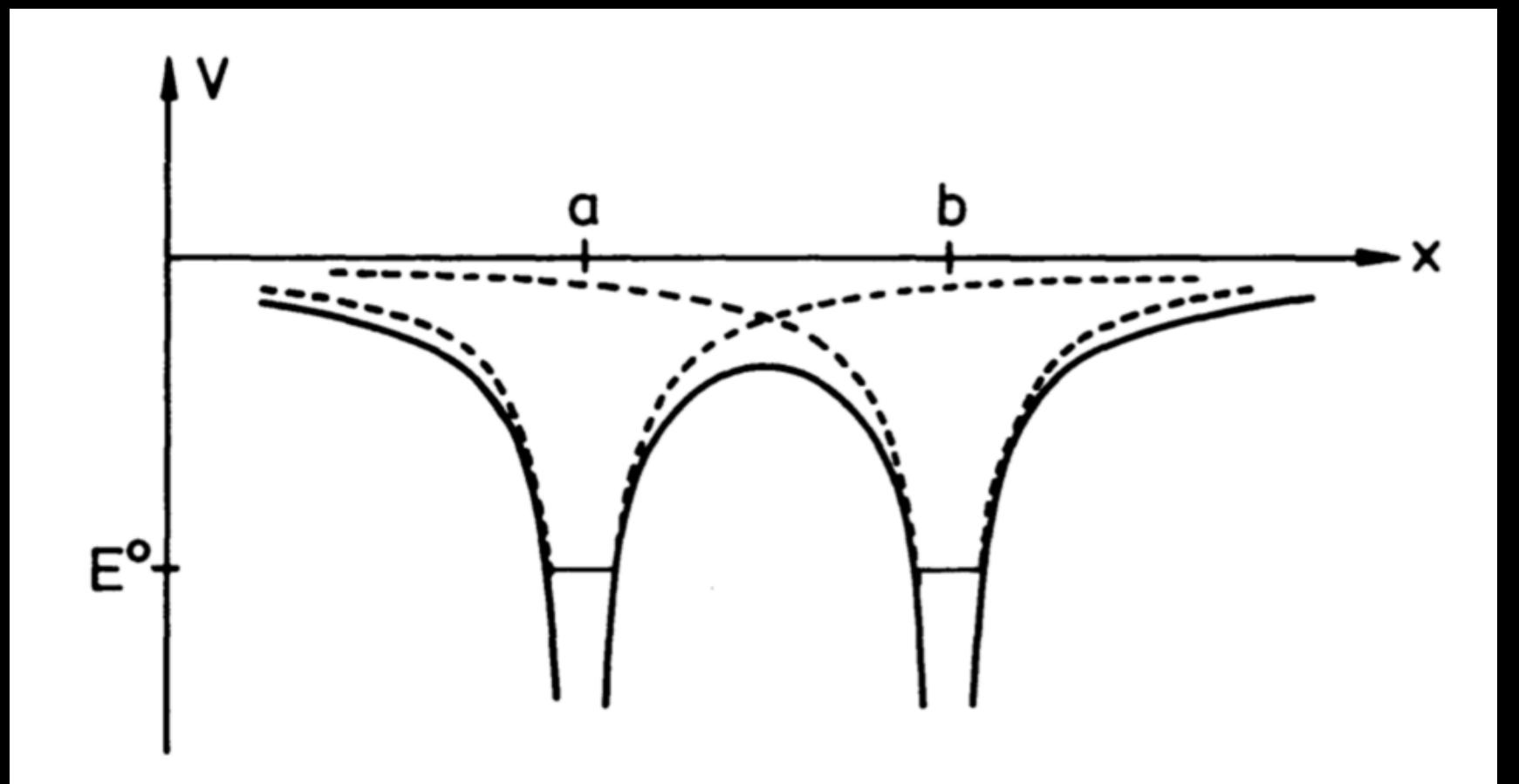
Starting point:  
Atomic Schrödinger Equation

$$\hat{H}_\alpha \phi_\alpha(\mathbf{r}_\alpha) = \left( -\frac{\hbar^2}{2m_0} \nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_\alpha} \right) \phi_\alpha(\mathbf{r}_\alpha) = E_\alpha^0 \phi_\alpha(\mathbf{r}_\alpha)$$

$\alpha = a, b$

$$E_a^0 = E_b^0 = E^0$$





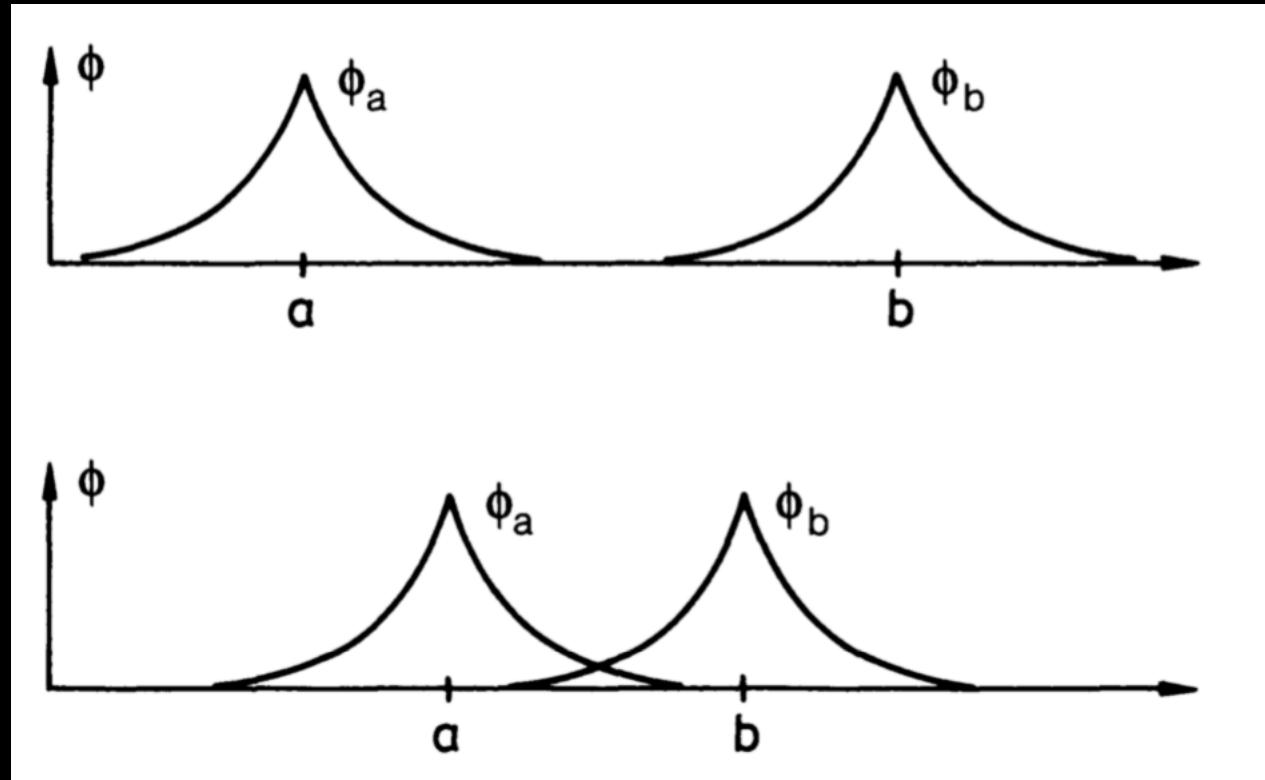
## Molecular Schrödinger Equation

$$\left( -\frac{\hbar^2}{2m_0} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} \right) \psi(\mathbf{r}_a, \mathbf{r}_b) = E \psi(\mathbf{r}_a, \mathbf{r}_b)$$

$$r_a = \sqrt{(R_{a,x} - x)^2 + (R_{a,y} - y)^2 + (R_{a,z} - z)^2}$$

$$r_b = \sqrt{(R_{b,x} - x)^2 + (R_{b,y} - y)^2 + (R_{b,z} - z)^2}$$

Guess:  
Use atomic wave functions  
as building blocks!



The atomic wave  
functions used  
here are also called  
*orbitals*.

$$\hat{H}_a$$

$$\hat{H}_b$$

$E^0$                                    $E^0$   
 $\phi_a$                                    $\phi_b$

$$\psi = c_a \phi_a + c_b \phi_b$$

$$= E(c_a \phi_a + c_b \phi_b)$$

$$\left( -\frac{\hbar^2}{2m_0} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} \right) c_a \phi_a +$$

$$\left( -\frac{\hbar^2}{2m_0} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_b} - \frac{e^2}{4\pi\epsilon_0 r_a} \right) c_b \phi_b$$

That's one small  
step for a man,  
one giant leap  
for mankind.

–Neil Armstrong, 1969



"That's one small step for (a) man;  
one giant leap for mankind."

– Neil Armstrong - July 20, 1969

$$\left( \underbrace{E^0 - E}_{\Delta E} - \frac{e^2}{4\pi\epsilon_0 r_b} \right) c_a \phi_a + \left( \underbrace{E^0 - E}_{\Delta E} - \frac{e^2}{4\pi\epsilon_0 r_a} \right) c_b \phi_b = 0$$

Left multiply  $\langle a | \mathbf{r} \rangle$  (suppose we're using real functions):

$$C, D \in \mathbb{R}$$

$$\langle a | \mathbf{r} \rangle = \phi_a^*(\mathbf{r})$$

$$\langle \phi_a | \phi_b \rangle = S \neq 0 \quad \langle a | \frac{-e^2}{4\pi\epsilon_0 r_b} | a \rangle = C \quad \langle a | \frac{-e^2}{4\pi\epsilon_0 r_a} | b \rangle = D$$

$$\Delta E c_a + C c_a + \Delta E S c_b + D c_b = 0 \quad \langle a | \hat{O} | b \rangle \equiv \int d\mathbf{r} \phi_a^*(\mathbf{r}) \hat{O} \phi_b(\mathbf{r})$$

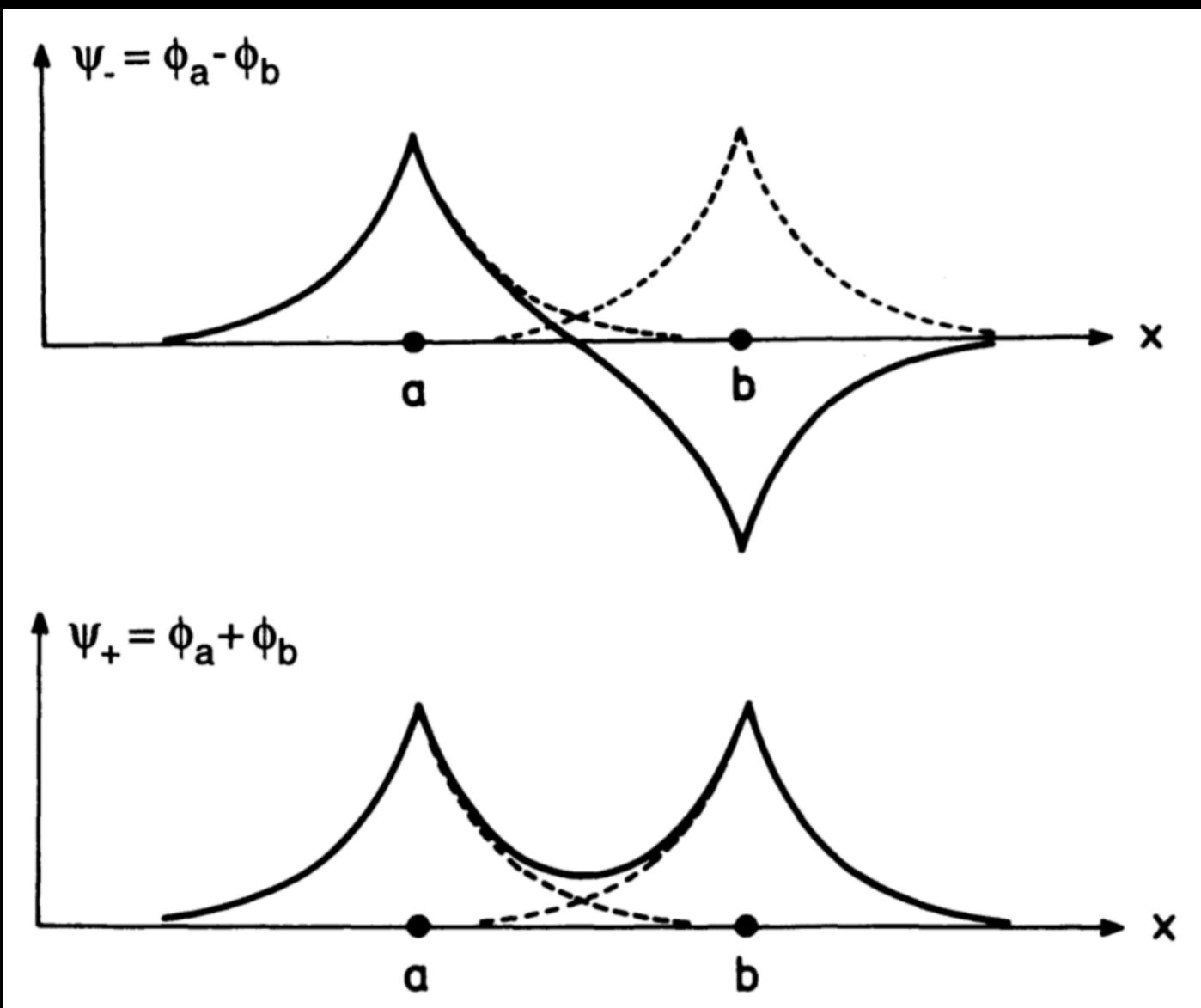
$$(\Delta E + C)c_a + (\Delta E S + D)c_b = 0$$

Left multiply  $\langle b | \mathbf{r} \rangle$ :

$$(\Delta E S + D)c_a + (\Delta E + C)c_b = 0$$

$$(\Delta E + C)c_a + (\Delta E S + D)c_b = 0$$

$$(\Delta E S + D)c_a + (\Delta E + C)c_b = 0$$

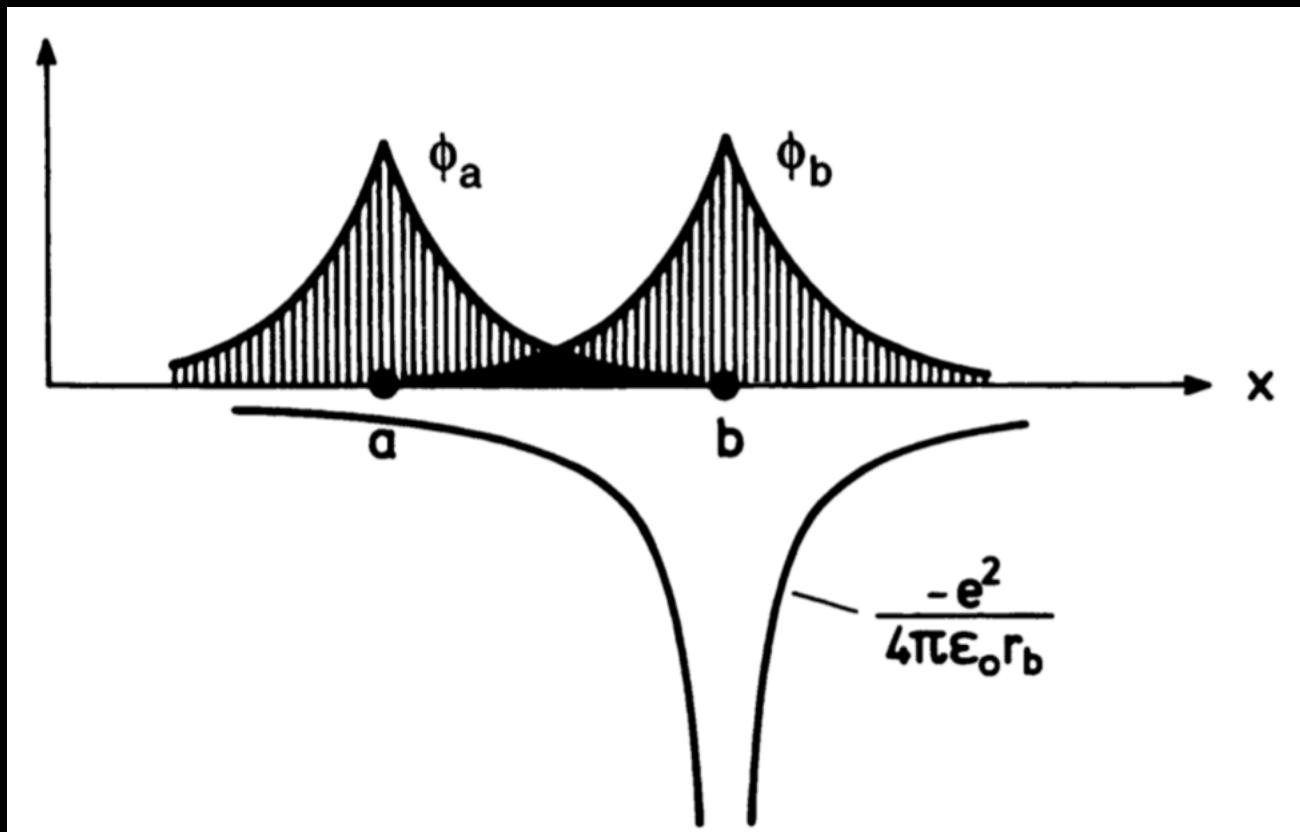
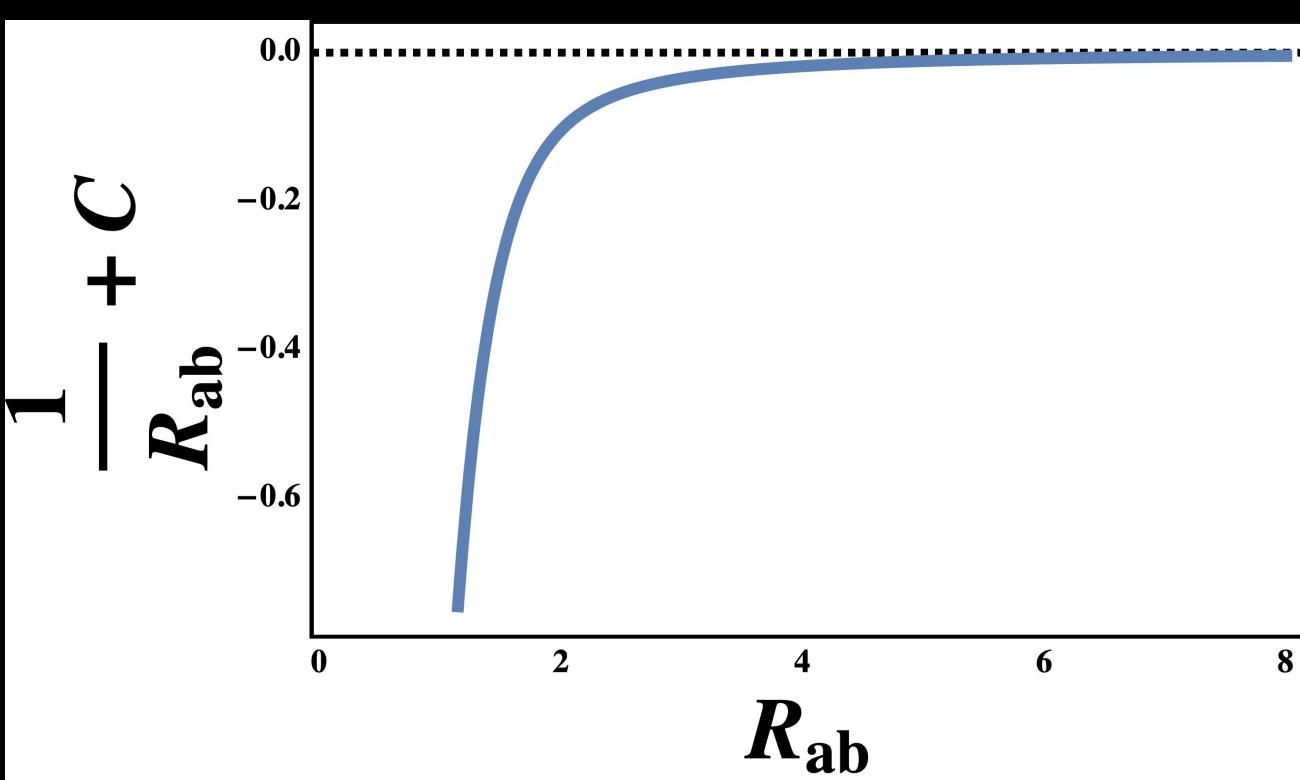
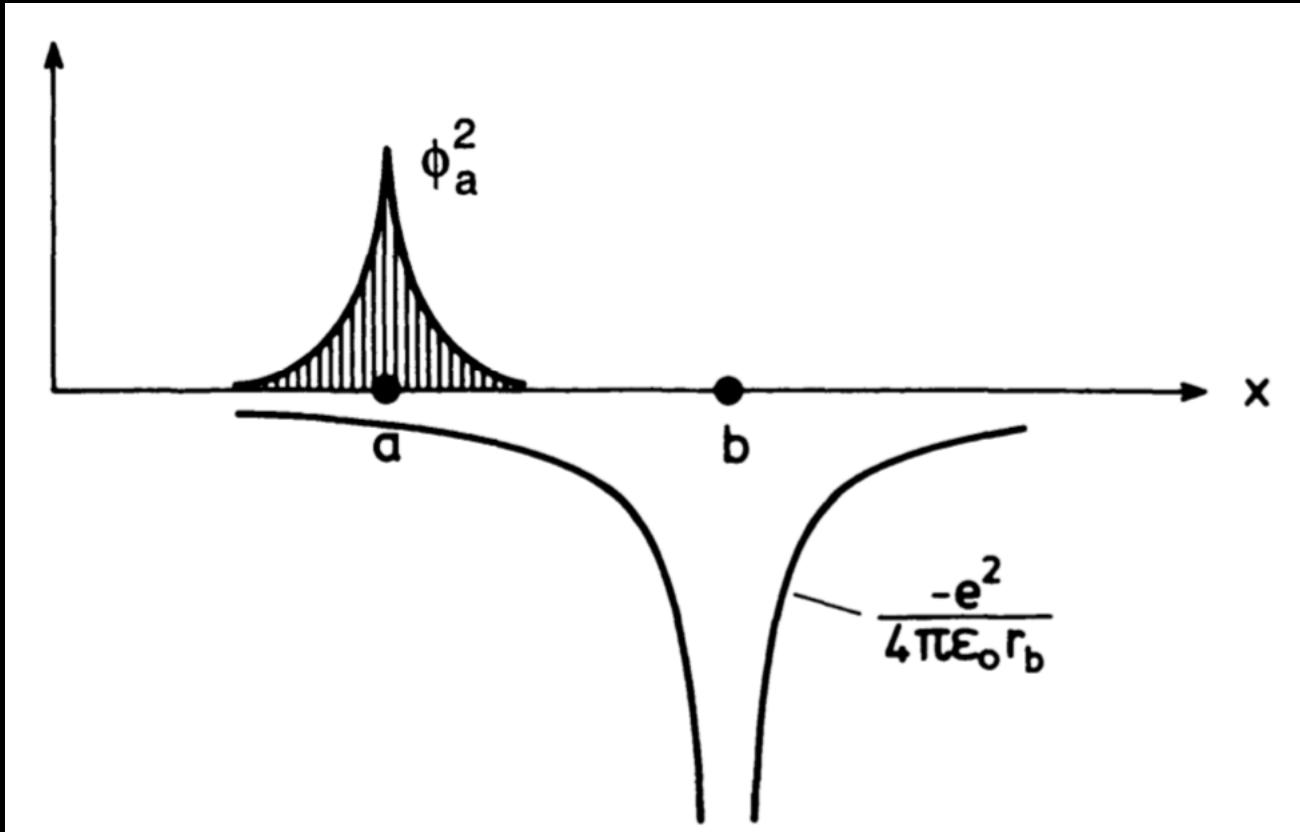


$$\rightarrow (\Delta E S + D)^2 - (\Delta E + C)^2 = 0$$

$$\Delta E_1 = E^0 + \frac{C - D}{1 - S}$$

$$\Delta E_2 = E^0 + \frac{C + D}{1 + S}$$

Here  $S$  is always small. So in later discussion, we can omit it.



$$\langle a | \frac{-e^2}{4\pi\epsilon_0 r_b} | a \rangle = C$$

$$\mathbf{r}_a = \mathbf{R}_{ab} + \mathbf{r}_b$$

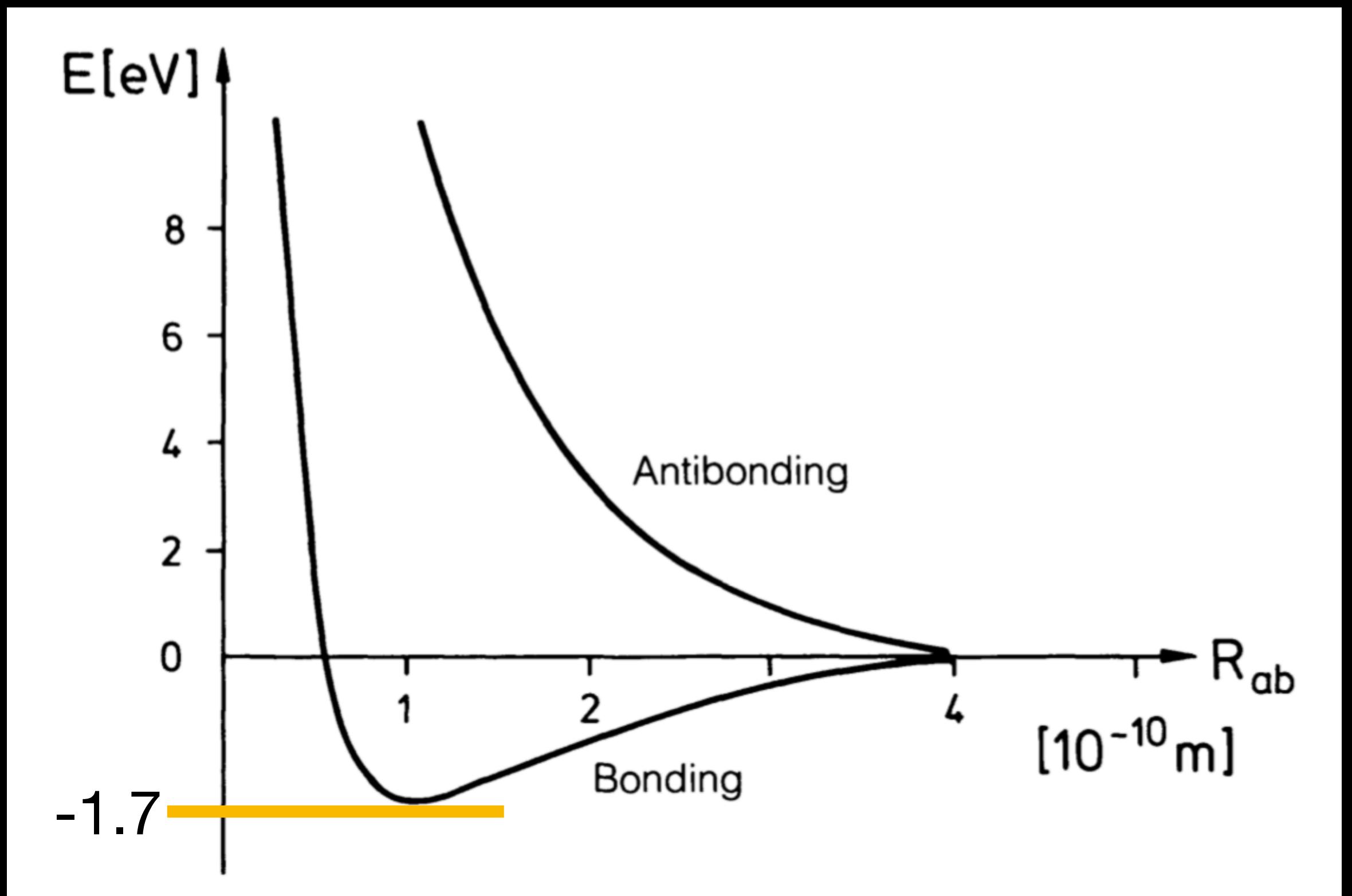
$$\mathbf{r}_b = \mathbf{r}_a - \mathbf{R}_{ab}$$

$$\phi_a(r) \propto e^{-\kappa r} \quad \frac{1}{r_b} = \frac{1}{|\mathbf{r}_a - \mathbf{R}_{ab}|} \approx \frac{1}{R_{ab}} \left(1 + \frac{r_b}{R_{ab}}\right)$$

When  $R_{ab}$  is large,  $C \approx -\frac{e^2}{4\pi\epsilon_0 R_{ab}}$ , this term counters the repulsion between the two protons.

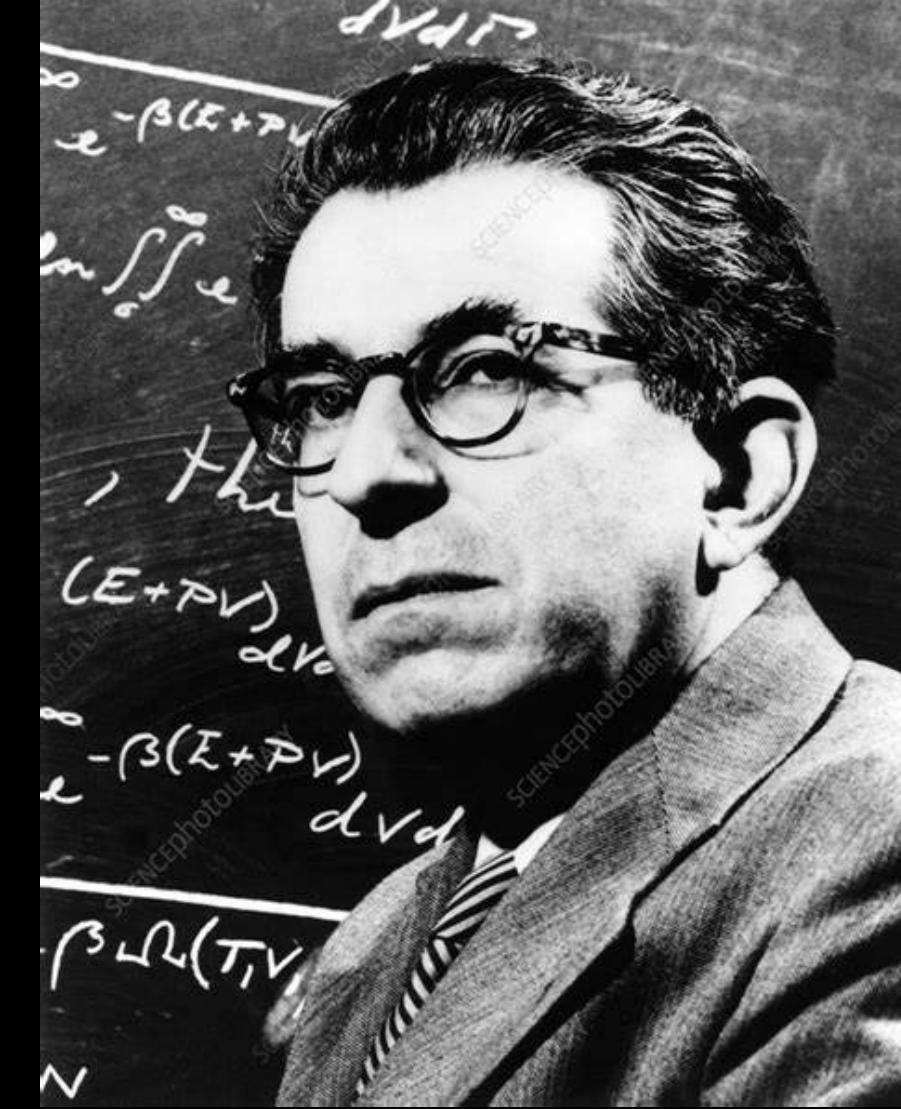
$$\langle a | \frac{-e^2}{4\pi\epsilon_0 r_a} | b \rangle = D$$

So the bonding mainly comes from the *exchange* term  $D$ , a *pure quantum* effect.



Experimental value:  $-2.65$  eV

|       | eV    | kcal/mol |
|-------|-------|----------|
| Calc. | -1.7  | -39.2    |
| Expr. | -2.65 | -61.1    |

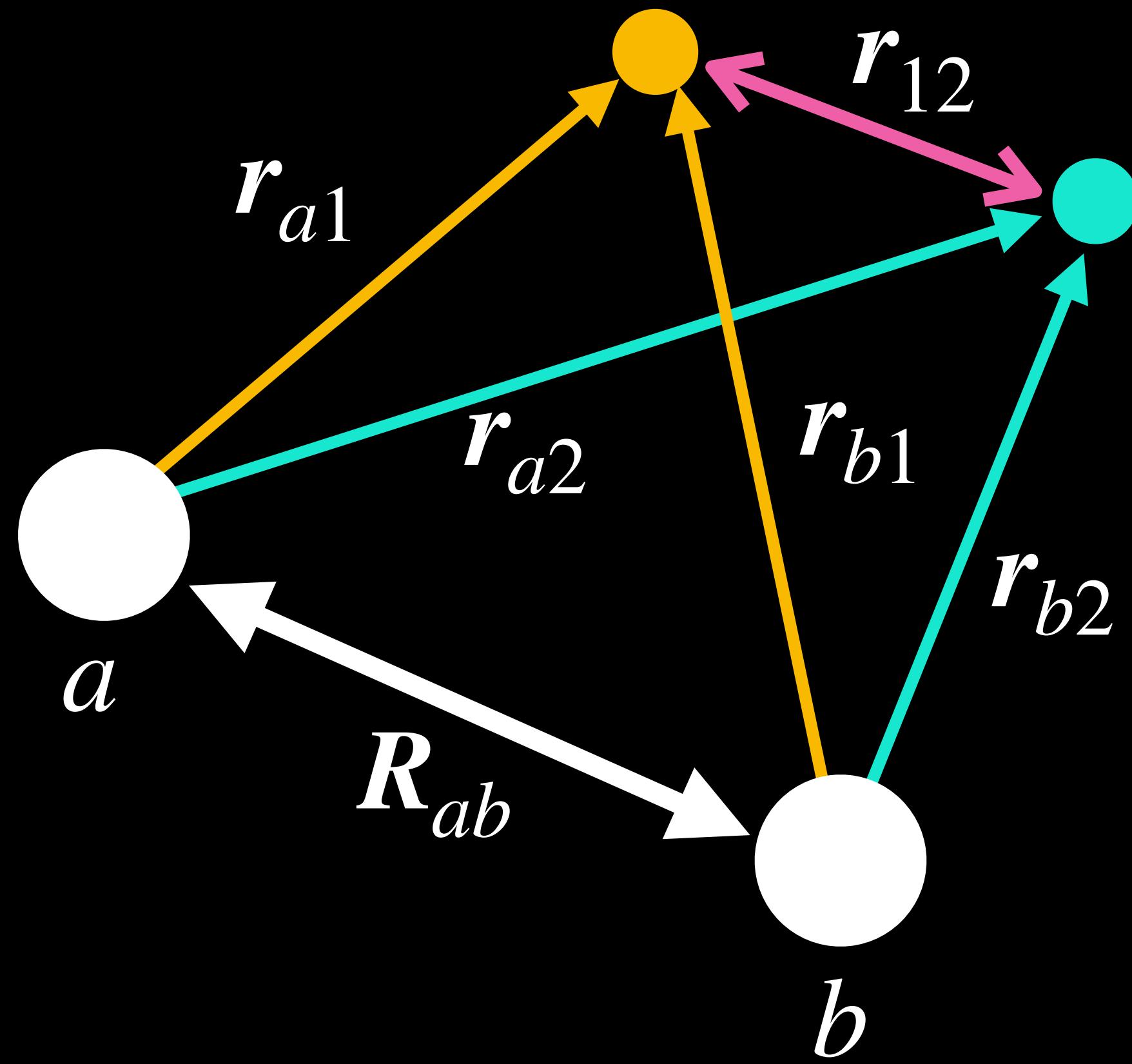


# Step even further: hydrogen molecule

**Walter Heinrich Heitler,**  
( 2 January 1904 - 15 November 1981)  
German physicist

**Fritz Wolfgang London,**  
(March 7, 1900 - March 30, 1954)  
German American physicist





$$\hat{H} = \begin{matrix} -\frac{\hbar^2}{2m_0}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0 r_{a_1}} & \boxed{-\frac{\hbar^2}{2m_0}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_{b_2}}} \\ \hline \frac{e^2}{4\pi\epsilon_0 r_{b_1}} & \frac{e^2}{4\pi\epsilon_0 r_{a_2}} + \frac{e^2}{4\pi\epsilon_0 R_{ab}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \end{matrix}$$

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2)$$

$$\left( -\frac{\hbar^2}{2m_0}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0 r_{a_1}} \right)\phi_a(\mathbf{r}_1) = E^0\phi_a(\mathbf{r}_1)$$

$$\left( -\frac{\hbar^2}{2m_0}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_{b_2}} \right)\phi_b(\mathbf{r}_2) = E^0\phi_b(\mathbf{r}_2)$$

# Pauli exclusion principle

The principle that two identical fermions cannot occupy the same quantum state in a body such as an atom.

— — Collins Encyclopedia



First, we need to consider the spin.

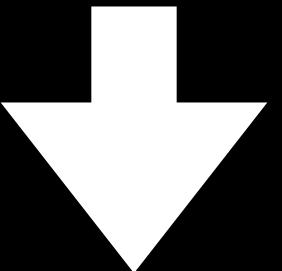
$$\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) \rightarrow \phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)\alpha(1)\alpha(2)$$

$$\langle \alpha(i) | \alpha(j) \rangle = \delta_{ij}$$

$$\langle \beta(i) | \beta(j) \rangle = \delta_{ij}$$

$$\langle \alpha(i) | \beta(j) \rangle = 0$$

But the Hartree product does not fulfill the Pauli exclusion principle.



$$\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)\alpha(1)\alpha(2) - \phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)\alpha(2)\alpha(1)$$

$$\Psi = \alpha(1)\alpha(2)\Psi_u(\mathbf{r}_1, \mathbf{r}_2) = \alpha(1)\alpha(2)[\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) - \phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)]$$

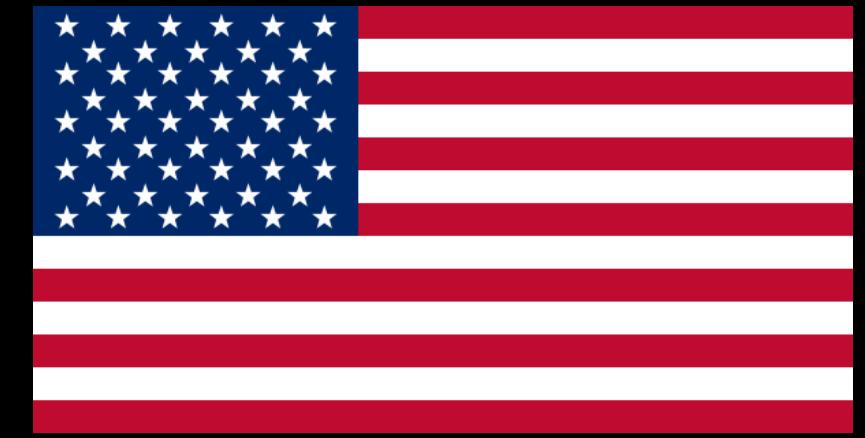


u: ungrade (Germany, odd)  
g: grade (Germany, even)

# Slater determinant

$$\Psi \propto \begin{vmatrix} \phi_a(\mathbf{r}_1)\alpha(1) & \phi_a(\mathbf{r}_2)\alpha(2) \\ \phi_b(\mathbf{r}_1)\alpha(1) & \phi_b(\mathbf{r}_2)\alpha(2) \end{vmatrix}$$

Standard tool for describing fermions.



John C. Slater

(1900-1976)

# All possibilities

$$\Psi = f_{\text{spin}}(1,2) \Psi_{g \text{ or } u}(\mathbf{r}_1, \mathbf{r}_2)$$

$$\Psi = \alpha(1)\alpha(2) \Psi_u(\mathbf{r}_1, \mathbf{r}_2)$$

$$\Psi = \beta(1)\beta(2) \Psi_u(\mathbf{r}_1, \mathbf{r}_2)$$

$$\Psi = \frac{1}{2} (\alpha(1)\beta(2) + \alpha(2)\beta(1)) \Psi_u(\mathbf{r}_1, \mathbf{r}_2)$$

Triplet

$$\Psi = \frac{1}{2} (\alpha(1)\beta(2) - \alpha(2)\beta(1)) [\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) + \phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)]$$

Singlet

$$= \frac{1}{2} (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \Psi_g(\mathbf{r}_1, \mathbf{r}_2)$$

# Heitler & London method

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2)$$

Since there is no spin term in  $\hat{H}$ , we can just use  $\Psi_g$  and  $\Psi_u$  as trial solutions.

Here we use a concise notation, fix the first term as the function containing the position of the first electron, and the second term as the function containing the second electron.

$$\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) - \phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2) \equiv |ab\rangle - |ba\rangle$$

$$\langle \Psi | \Psi \rangle \equiv \int \int |\Psi|^2 d^3r_1 d^3r_2 \qquad \qquad d^3r \equiv dx dy dz = r^2 \sin \theta dr d\theta d\phi$$

$$\begin{aligned}\langle \Psi | \Psi \rangle &= \left[ \langle ab | \pm \langle ba | \right] \left[ | ab \rangle \pm | ba \rangle \right] \\ &= \langle ab | ab \rangle \pm \langle ab | ba \rangle \pm \langle ba | ab \rangle + \langle ba | ba \rangle\end{aligned}$$

$$\langle ab | ab \rangle = \langle a | a \rangle \langle b | b \rangle = 1 = \langle ba | ba \rangle$$

$$\langle ab | ba \rangle = \langle ba | ab \rangle = \langle a | b \rangle \langle b | a \rangle = |S|^2 = S^2$$

$$\boxed{\langle \Psi | \Psi \rangle = 2(1 \pm S^2)}$$

$$\frac{\langle \Psi_{g\,\mathrm{or}\,u}|\hat{H}|\Psi_{g\,\mathrm{or}\,u}\rangle}{\langle\Psi|\Psi\rangle}\geq E_\mathrm{ground}$$

$$\begin{aligned}&\left(\langle ab| \pm \langle ba|\right) \hat{H} \left( |ab\rangle \pm |ba\rangle\right)\\&=2\langle ab|\hat{H}|ab\rangle \pm 2\langle ab|\hat{H}|ba\rangle\end{aligned}$$

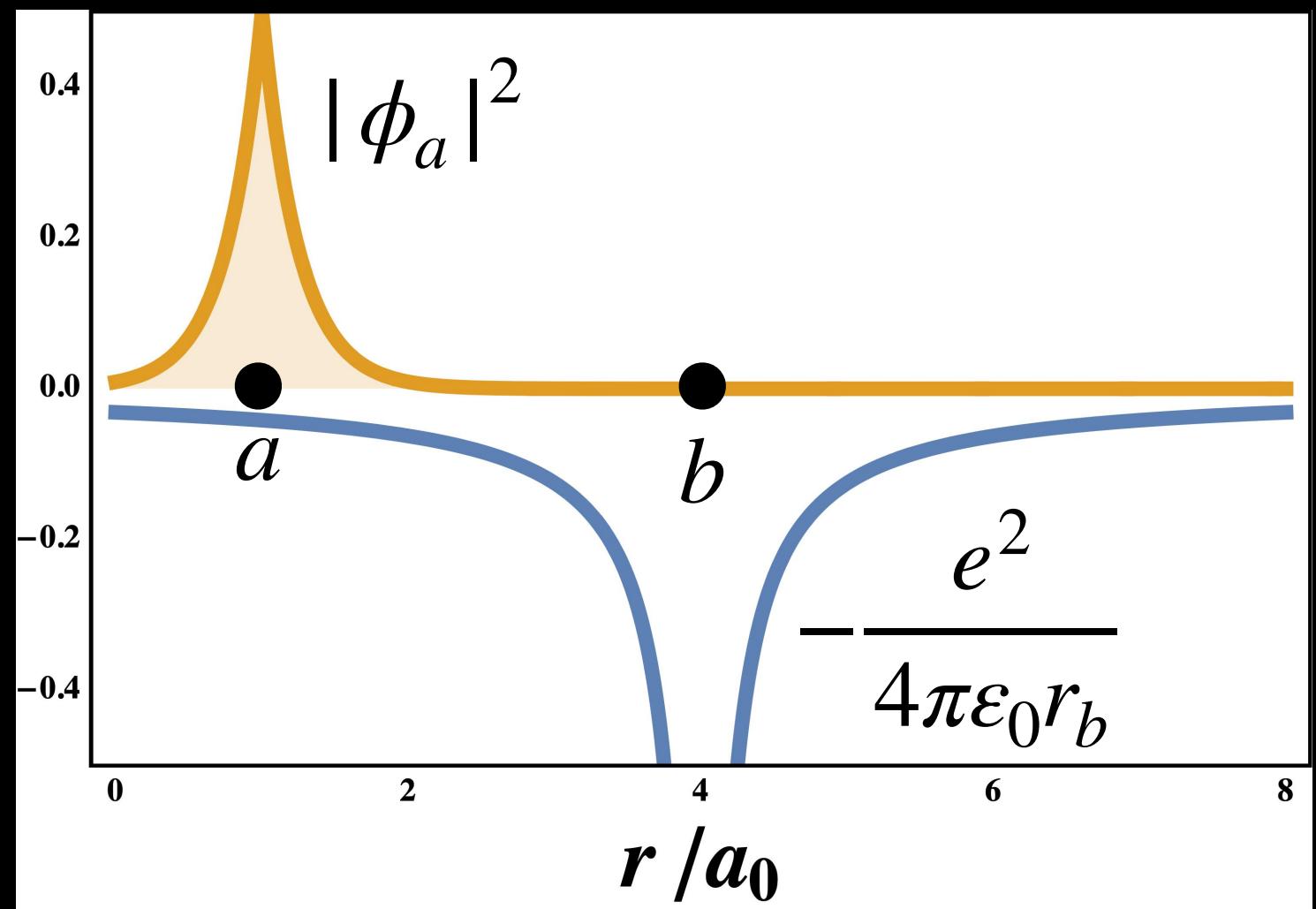
$$\langle ab|\hat{H}|ab\rangle$$

$$=\int\int\frac{\phi_a^*\phi_b^*}{\uparrow}\left[2E^0-\frac{e^2}{4\pi\varepsilon_0 r_{b_1}}-\frac{e^2}{4\pi\varepsilon_0 r_{a_2}}+\frac{e^2}{4\pi\varepsilon_0 R_{ab}}+\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right]\phi_a\phi_b\mathrm{d}^3r_1\mathrm{d}^3r_2$$

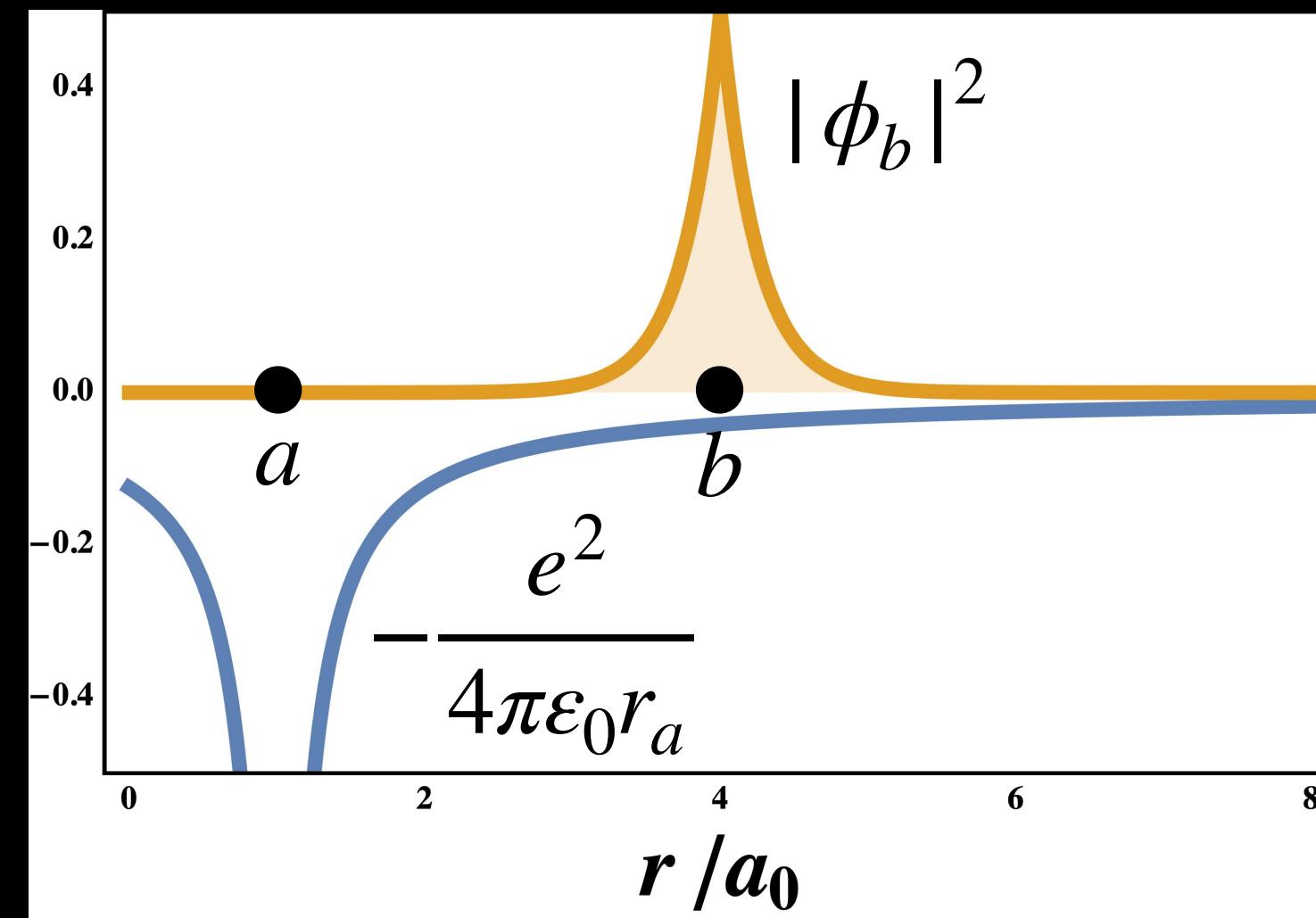
$$\phi_a^*(\boldsymbol{r}_1)\phi_b^*(\boldsymbol{r}_2)$$

$$\int \phi_a^*(\mathbf{r}_1) \left[ -\frac{e^2}{4\pi\epsilon_0 r_{b_1}} \right] \phi_a(\mathbf{r}_1) d^3r_1 = C = \int \phi_b^*(\mathbf{r}_2) \left[ -\frac{e^2}{4\pi\epsilon_0 r_{a_2}} \right] \phi_b(\mathbf{r}_2) d^3r_2$$

Coulomb interaction energy of nucleus ***b*** with electron **1** in state ***a***.



Coulomb interaction energy of nucleus ***a*** with electron **2** in state ***b***.



$$\langle ab|\frac{e^2}{4\pi\varepsilon_0 R_{ab}}|ab\rangle=E_{\rm RN}$$

$$\langle ab|\frac{e^2}{4\pi\varepsilon_0 r_{12}}|ab\rangle=E_{\rm CE}$$

$$E_{\text{part}\,1}=2E_0+2C+E_{\text{RN}}+E_{\text{CE}}$$

$$\langle ab | \hat{H} | ba \rangle$$

$$= \int \int \phi_a^* \phi_b^* \left[ 2E^0 - \frac{e^2}{4\pi\epsilon_0 r_{b_1}} - \frac{e^2}{4\pi\epsilon_0 r_{a_2}} + \frac{e^2}{4\pi\epsilon_0 R_{ab}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right] \phi_b \phi_a d^3r_1 d^3r_2$$

$$\int \int \phi_a^* \phi_b^* 2E^0 \phi_b \phi_a d^3r_1 d^3r_2 = 2E^0 S$$

$$\langle a | \frac{-e^2}{4\pi\epsilon_0 r_{b1}} | b \rangle \langle b | a \rangle = DS$$

$$\langle a | b \rangle \langle b | \frac{-e^2}{4\pi\epsilon_0 r_{a2}} | a \rangle = DS$$

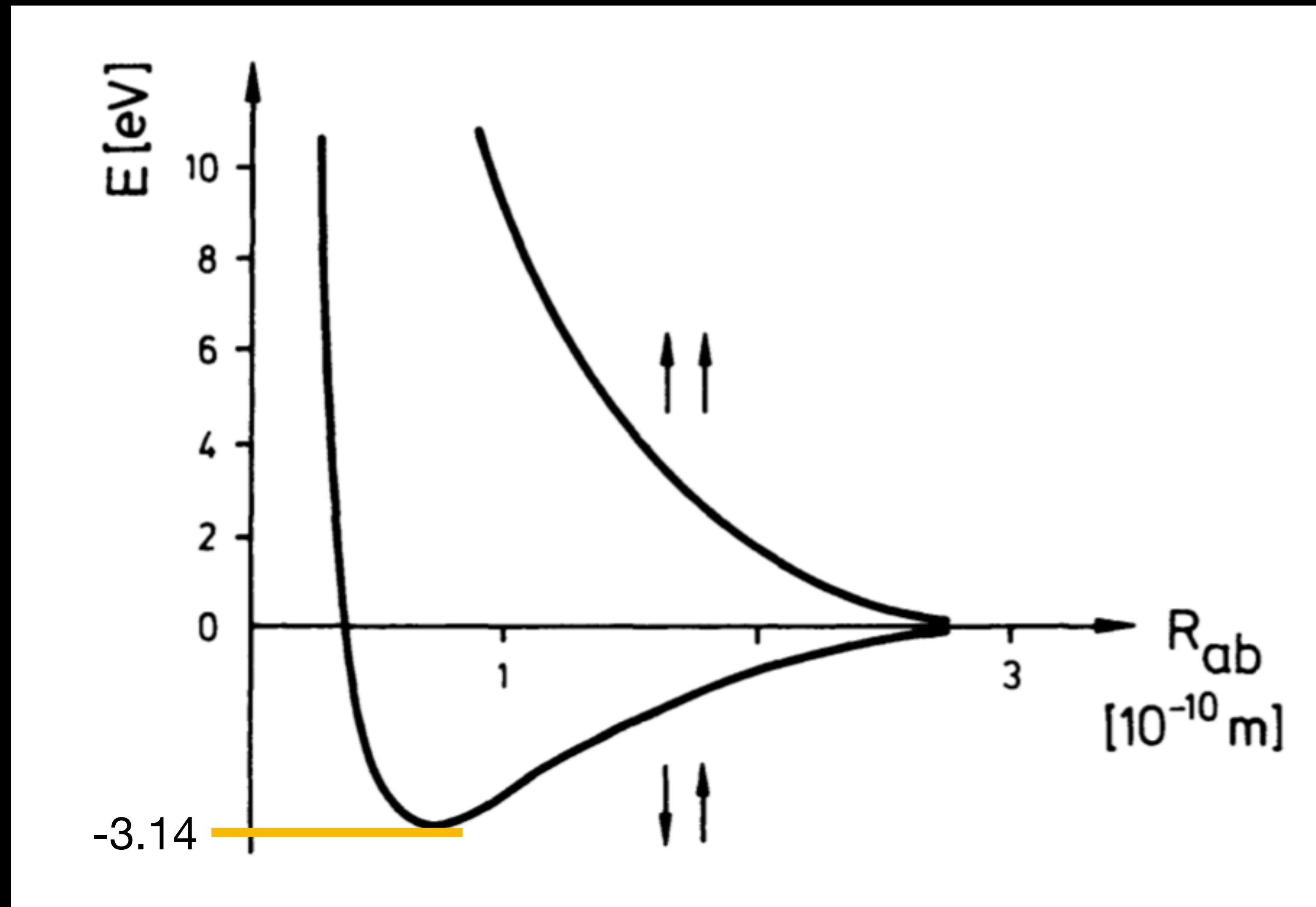
$$\langle ab | \frac{e^2}{4\pi\epsilon_0 R_{ab}} | ba \rangle = E_{\text{RN}} S^2$$

$$\langle ab | \frac{e^2}{4\pi\epsilon_0 r_{12}} | ba \rangle = E_{\text{CE}}$$

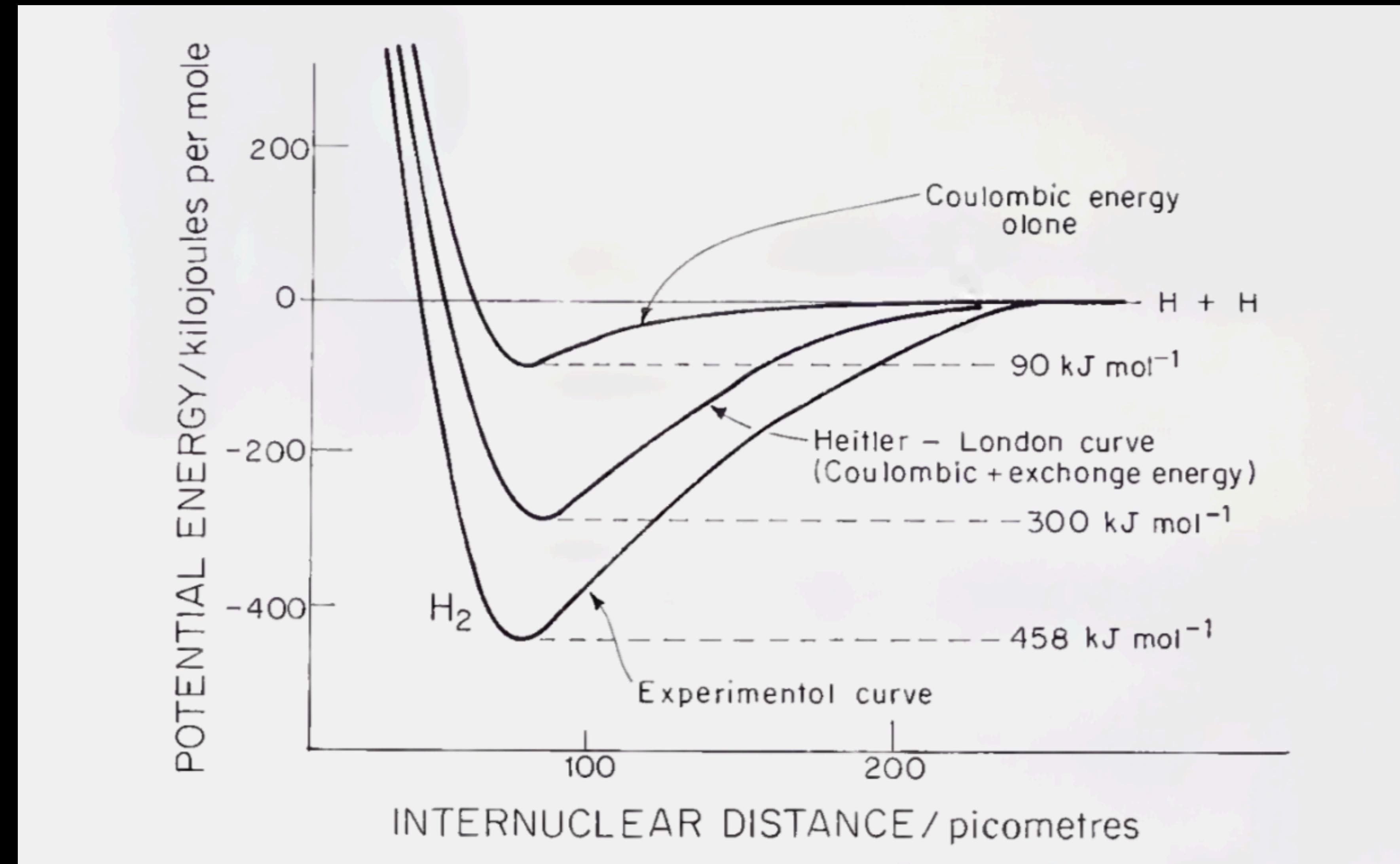
$$E_{\text{part}\,1}=2E_0+2C+E_{\text{RI}}+E_{\text{RN}}$$

$$E_{\text{part}\,2}=2E_0S^2+2DS+E_{\text{RN}}S^2+E_{\text{CE}}$$

$$\begin{aligned} E_{g,u} &= \frac{\langle\Psi_{g\,\mathrm{or}\,u}|\hat{H}|\Psi_{g\,\mathrm{or}\,u}\rangle}{\langle\Psi|\Psi\rangle} = \frac{2\langle ab|\hat{H}|ab\rangle}{2(1\pm S^2)}\pm\frac{2\langle ab|\hat{H}|ba\rangle}{2(1\pm S^2)} \\ &= \frac{E_{\text{part}\,1}\pm E_{\text{part}\,2}}{1\pm S^2} \\ &= 2E^0+\frac{2C+E_{\text{RI}}}{1\pm S^2}\pm\frac{2DS+E_{\text{CE}}}{1\pm S^2}+E_{\text{RN}} \end{aligned}$$



Experimental value:  $-4.48$  eV



Actually, the *exchange* interaction is the driving force of bonding!

Keith Ladler, *The World of Physical Chemistry*, Oxford University Press, 1995

# Covalent-Ion resonance

Till now, what wave function we used is one electron move near one atom, and another electron move near another atom separately.

$$\psi_{\text{cov}} = N [\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) \pm \phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)]$$

But still there is some possibility the electrons all reside one single nucleus. And we can assume the final wave function is the linear combination of both.

$$\psi_{\text{ion}} = N' [\phi_a(\mathbf{r}_1)\phi_a(\mathbf{r}_2) \pm \phi_b(\mathbf{r}_1)\phi_b(\mathbf{r}_2)]$$

$$\Psi = \psi_{\text{cov}} + c\psi_{\text{ion}}$$

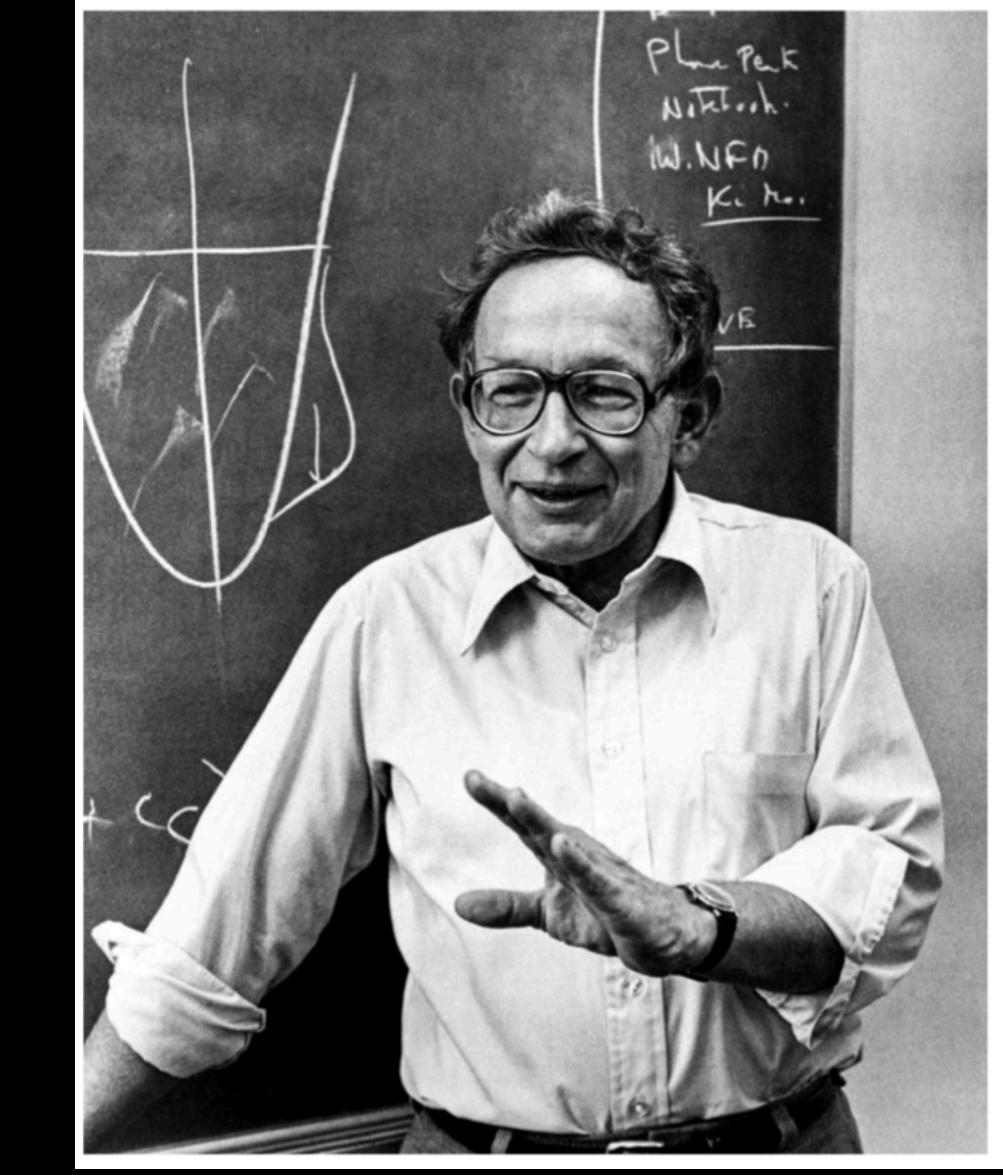
# Influence in Condensed Matter Physics

## Resonating VB



Materials Research Bulletin

Volume 8, Issue 2, February 1973, Pages 153-160



Resonating valence bonds: A new kind of insulator?

P.W. Anderson <sup>a, b</sup>

### References

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# Hund-Mulliken-Bloch method

One at first ignores the fact that two electrons are present. Instead, we consider the motion of a **single electron in the field of the two nuclei** or, in other words, we begin with the solution of the hydrogen molecule-ion problem.

$$\psi_g(\mathbf{r}) = N [\phi_a(\mathbf{r}) + \phi_b(\mathbf{r})] \quad \Psi(\mathbf{x}_1, \mathbf{x}_2) = \psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

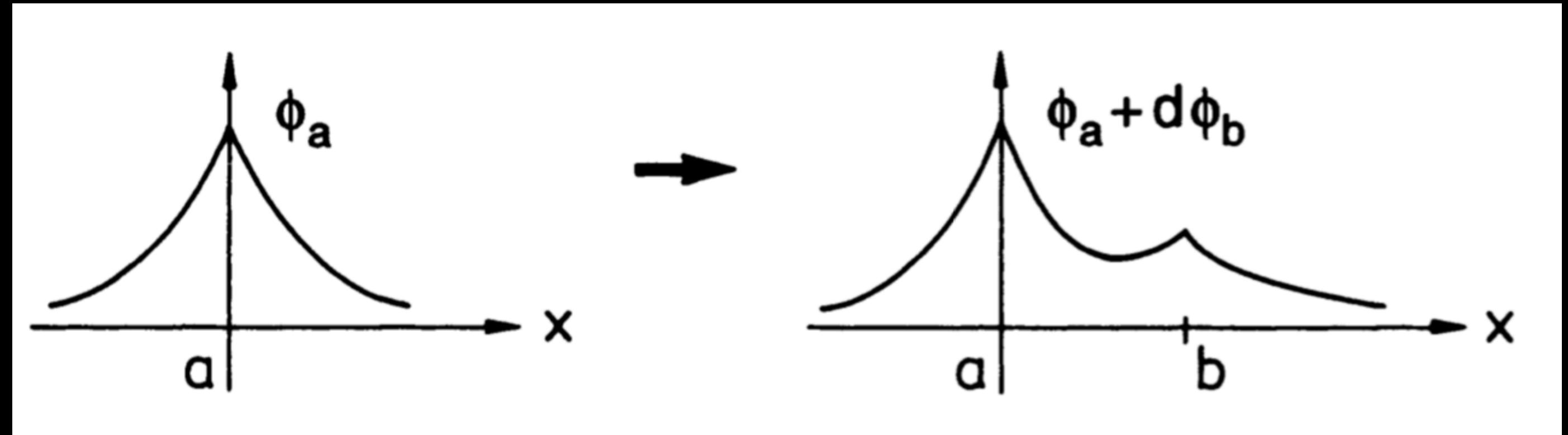
The energy from Hund-Mullikan-Bloch method is higher than that from Heitler-London's, but it's a starting point of calculating multi-electron molecules. This is the thought of **LCAO: Linear Combination of Atomic Orbital**.

# Outlines of MO

In this type of theory, the A and B atoms are brought together firstly to become a ‘united atom’ AB. Then the electrons are fed one by one into the AB molecule.

This thought is firstly given by Sir John Edward Lennard-Jones (1894-1954). The MO method is proposed to explain molecular spectra.

The contributors including Sir Lennard-Jones, Hund, Mullikan, Gerhard Herzberg, Felix Bloch (extended this thought into investigations of solids), Charles A. Coulson, Erick/Walter Hückel (they are brothers) and so on.



$$\phi_a \rightarrow \phi_a + d\phi_b$$

$$\phi_b \rightarrow \phi_b + d\phi_a$$

$$\begin{aligned}
 \Psi_g(\mathbf{r}_1, \mathbf{r}_2) &= [\phi_a(\mathbf{r}_1) + d\phi_b(\mathbf{r}_1)] [\phi_b(\mathbf{r}_2) + d\phi_a(\mathbf{r}_2)] + [\phi_b(\mathbf{r}_1) + d\phi_a(\mathbf{r}_1)] [\phi_a(\mathbf{r}_2) + d\phi_b(\mathbf{r}_2)] \\
 &= (1 + d^2)[|ab\rangle + |ba\rangle] + 2d[|aa\rangle + |bb\rangle] \\
 &\propto \psi_{\text{cov}} + c\psi_{\text{ion}}
 \end{aligned}$$

$$c = \frac{2d}{1 + d^2}$$

$$\begin{aligned}
& \text{Kinetic energy (nucl. and el.)} && \text{Coulomb repulsion (el.-el.)} \\
\hat{H} = & \underbrace{\sum_{i=1}^K \text{nuclei} - \frac{\hbar^2}{2m_i} \nabla_{\mathbf{r}_i}^2}_{\text{Coulomb attraction (el.-nucl.)}} + \underbrace{\sum_{j=1}^N \text{electrons} - \frac{\hbar^2}{2m_i} \nabla_{\mathbf{r}_j}^2}_{\text{Coulomb repulsion (nucl.-nucl.)}} + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{k=1}^N \sum_{l>k}^N \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_l|} \\
& - \frac{1}{4\pi\epsilon_0} \sum_{m=1}^K \sum_{n=1}^N \frac{Z_m e^2}{|\mathbf{r}_n - \mathbf{R}_m|} + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{o=1}^K \sum_{p>0}^K \frac{Z_o Z_p e^2}{|\mathbf{R}_o - \mathbf{R}_k|} \quad (2)
\end{aligned}$$

# Multi-electron molecules: H-F

General method

# Preliminary

# Setup

There are  $N$  electrons:

$$\mathbf{r}_j, \quad j = 1, 2, \dots, N$$

There are  $M$  nuclei:

$$\mathbf{R}_K, Z_K, \quad K = 1, 2, \dots, M$$

$$V(\mathbf{r}_j) = \sum_K V_K(\mathbf{r}_j)$$

$$V_K(\mathbf{r}_j) = -\frac{Z_K e^2}{4\pi\epsilon_0 |\mathbf{R}_K - \mathbf{r}_j|}$$

$$|\mathbf{R}_K - \mathbf{r}_j| = \sqrt{(X_K - x_j)^2 + (Y_K - y_j)^2 + (Z_K - z_j)^2}$$

# Hamiltonian

$$\hat{H}(\mathbf{r}_j) \equiv \hat{H}(j) = \frac{\hbar^2}{2m_0} \nabla_j^2 + V(\mathbf{r}_j)$$

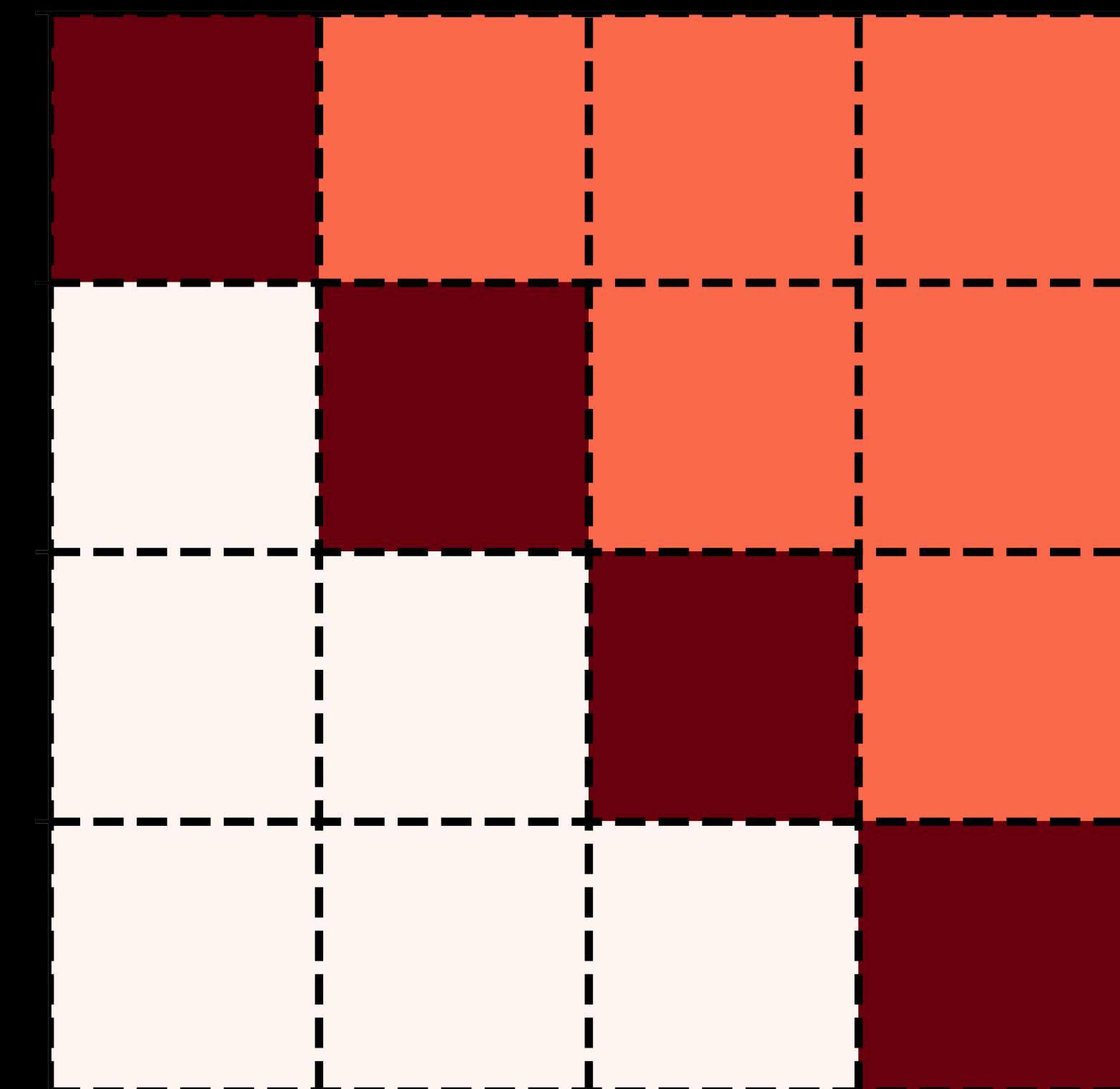
$$W_{jl} = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_j - \mathbf{r}_l|}$$

$$\hat{H}_{\text{int}} = \frac{1}{2} \sum_{j \neq l} W_{jl} = \sum_{j < l} W_{jl}$$

$$\hat{H} = \sum_j \hat{H}(j) + \hat{H}_{\text{int}}$$

Here we have neglected the spin-orbit interaction.

- Things must consider:
1. Pauli exclusion principle.
  2. Electrons interact each other.



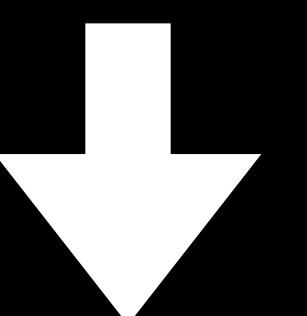
# Distraction: Linear Variational Principle

From previous discussion on variational principle, there is no *a priori* choice of the trial basis:  $|\tilde{\Phi}\rangle$ . So we need a systematical guess for it.

$$|\tilde{\Phi}\rangle = \sum_{i=1}^N c_i |\Psi_i\rangle \quad \text{Known basis}$$

Setup:

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij} \quad \langle \Psi_i | \hat{H} | \Psi_j \rangle = H_{ij} \quad \langle \tilde{\Phi} | \tilde{\Phi} \rangle = \sum_{ij} c_i c_j \langle \Psi_i | \Psi_j \rangle = \sum_i c_i^2 = 1$$



$$\langle \tilde{\Phi} | \hat{H} | \tilde{\Phi} \rangle = \sum_{ij} c_i c_j H_{ij}$$

In general, this is  
a real number

# Lagrange multiplier

Goal: optimize this summation:

$$\langle \tilde{\Phi} | \hat{H} | \tilde{\Phi} \rangle = \sum_{ij} c_i c_j H_{ij}$$

Restraint: orthonormalization

$$\langle \tilde{\Phi} | \tilde{\Phi} \rangle = \sum_{ij} c_i c_j \langle \Psi_i | \Psi_j \rangle = \sum_i c_i^2 = 1$$

$$\mathcal{L} = \langle \tilde{\Phi} | \hat{H} | \tilde{\Phi} \rangle - E(\langle \tilde{\Phi} | \tilde{\Phi} \rangle - 1) = \sum_{ij} c_i c_j H_{ij} - \tilde{E}(\sum_i c_i^2 - 1)$$

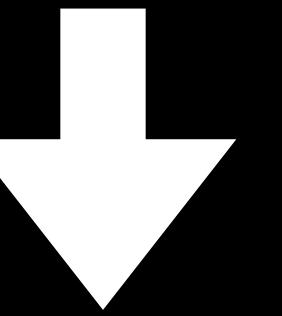
$$\frac{\partial}{\partial c_k} \mathcal{L} = 0, \quad k = 1, 2, \dots, N$$

$$\sum_j c_j H_{ij} - \tilde{E} c_i = 0$$

$$\sum_j c_j H_{ij} - \tilde{E} c_i = 0$$

Linear variational equation:  $Hc = \tilde{E}c$

$$Hc^\alpha = \tilde{E}_\alpha c^\alpha \quad \alpha = 0, 1, \dots, N-1$$



Introduce  $C$ :

$$C_{i\alpha} = c_i^\alpha$$

$$HC = C\tilde{E}$$

$$\tilde{E}_0 = \langle \tilde{\Phi}_0 | \hat{H} | \tilde{\Phi}_0 \rangle \geq E_0$$

# Atomic Units

| Physical quantity       | Conversion factor $X$           | Value of $X$ (SI)  |
|-------------------------|---------------------------------|--|
| Length                  | $a_0$                           | $5.2918 \times 10^{-11}$ m   |
| Mass                    | $m_e$                           | $9.1095 \times 10^{-31}$ kg  |
| Charge                  | $e$                             | $1.6022 \times 10^{-19}$ C   |
| Energy                  | $\mathcal{E}_a$                 | $4.3598 \times 10^{-18}$ J   |
| Angular momentum        | $\hbar$                         | $1.0546 \times 10^{-34}$ Js  |
| Electric dipole moment  | $ea_0$                          | $8.4784 \times 10^{-30}$ Cm  |
| Electric polarizability | $e^2 a_0^2 \mathcal{E}_a^{-1}$  | $1.6488 \times 10^{-41}$ C <sup>2</sup> m <sup>2</sup> J <sup>-1</sup> |
| Electric field          | $\mathcal{E}_a e^{-1} a_0^{-1}$ | $5.1423 \times 10^{11}$ V m <sup>-1</sup>                              |
| Wave function           | $a_0^{-3/2}$                    | $2.5978 \times 10^{15}$ m <sup>-3/2</sup>                              |

Attila Szabo & Neil Ostlund, *Modern Quantum Chemistry*, Dover, 1996

# Many electron Hamiltonian in a.u.

$$\hat{H} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}$$

# Spin Orbitals and Spatial Orbitals

|                          |  |
|--------------------------|--|
| <b>Orbital</b>           | A wave function for a single particle, such as electron.                                     |
| <b>Molecular Orbital</b> | A wave function of a electron in a molecule.   |
| <b>Spatial Orbital</b>   | A function of the position vector and describes the distribution density as its square norm. |
| <b>Spin Orbital</b>      | Spatial orbital multiplies a spin function, either spin-up or spin-down.                     |

In quantum mechanics one replaces the word ‘orbit’ with *orbital*, a word introduced by R. S. Mulliken who defined it in a simple way by saying that an orbital is as much like an orbit as quantum mechanics permits. More precisely, the word ‘orbital’ refers to a wavefunction that relates to a single electron associated with an atom or molecule.

Keith Ladler, *The World of Physical Chemistry*, Oxford University Press, 1995

$$\int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d^3r = \delta_{ij} \equiv \langle i | j \rangle$$

Spatial orbital

$$\chi(\mathbf{x}) = \begin{cases} \psi(\mathbf{r})\alpha(\omega) \\ \text{or} \\ \psi(\mathbf{r})\beta(\omega) \end{cases}$$

Spin orbital

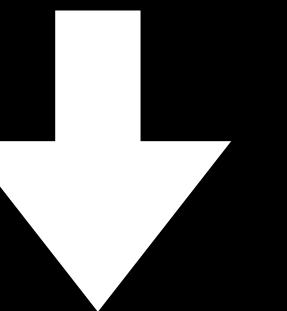
Given  $K$  spatial orbitals  $\{\psi_i | i = 1, 2, \dots, K\}$ , one can form a set of  $2K$  spin orbitals  $\{\chi_i | i = 1, 2, \dots, 2K\}$  as:

$$\left. \begin{array}{l} \chi_{2i-1}(\mathbf{x}) = \psi_i(\mathbf{r})\alpha(\omega) \\ \chi_{2i}(\mathbf{x}) = \psi_i(\mathbf{r})\beta(\omega) \end{array} \right\} i = 1, 2, \dots, K$$

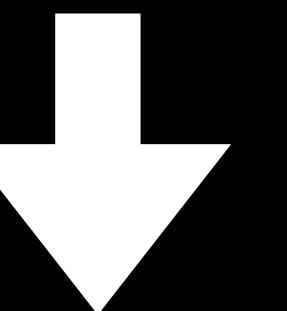
$$\langle \chi_i | \chi_j \rangle \equiv \int \chi_i^*(\mathbf{x}) \chi_j(\mathbf{x}) d\mathbf{x} = \delta_{ij}$$

# Hartree Product

$$\hat{H} = \sum_i \hat{H}(i) \quad \hat{H}(i)\chi_j(\mathbf{x}_i) = \varepsilon_j\chi_j(\mathbf{x}_i)$$



$$\Psi^{\text{HP}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N)$$



$$\hat{H}\Psi^{\text{HP}} = E\Psi^{\text{HP}} \quad E = \varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k$$

# Slater Determinant for many electron system

Recall the Slater determinant for H<sub>2</sub>:

$$\Psi \propto \begin{vmatrix} \phi_a(\mathbf{r}_1)\alpha(1) & \phi_a(\mathbf{r}_2)\alpha(2) \\ \phi_b(\mathbf{r}_1)\alpha(1) & \phi_b(\mathbf{r}_2)\alpha(2) \end{vmatrix}$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = (N!)^{-1/2} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \cdots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \cdots & \chi_k(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \cdots & \chi_k(\mathbf{x}_N) \end{vmatrix}$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = (N!)^{-1/2} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \cdots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \cdots & \chi_k(\mathbf{x}_2) \\ \vdots & \vdots & \cdots & \vdots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \cdots & \chi_k(\mathbf{x}_N) \end{vmatrix}$$

To learn second quantization from zero, one can resort to C.

Kittel, *Quantum Theory of Solids*, 2nd edition, 1987,  
Chapter 5.

$$= |\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N)\rangle$$

$$= |\chi_i\chi_j\cdots\chi_k\rangle = |ij\cdots k\rangle$$

$$= \hat{a}_i^\dagger \hat{a}_j^\dagger \cdots \hat{a}_k^\dagger |00\cdots 0\rangle$$

$$\left\{ \hat{a}_\alpha^\dagger, \hat{a}_\beta^\dagger \right\} = 0$$

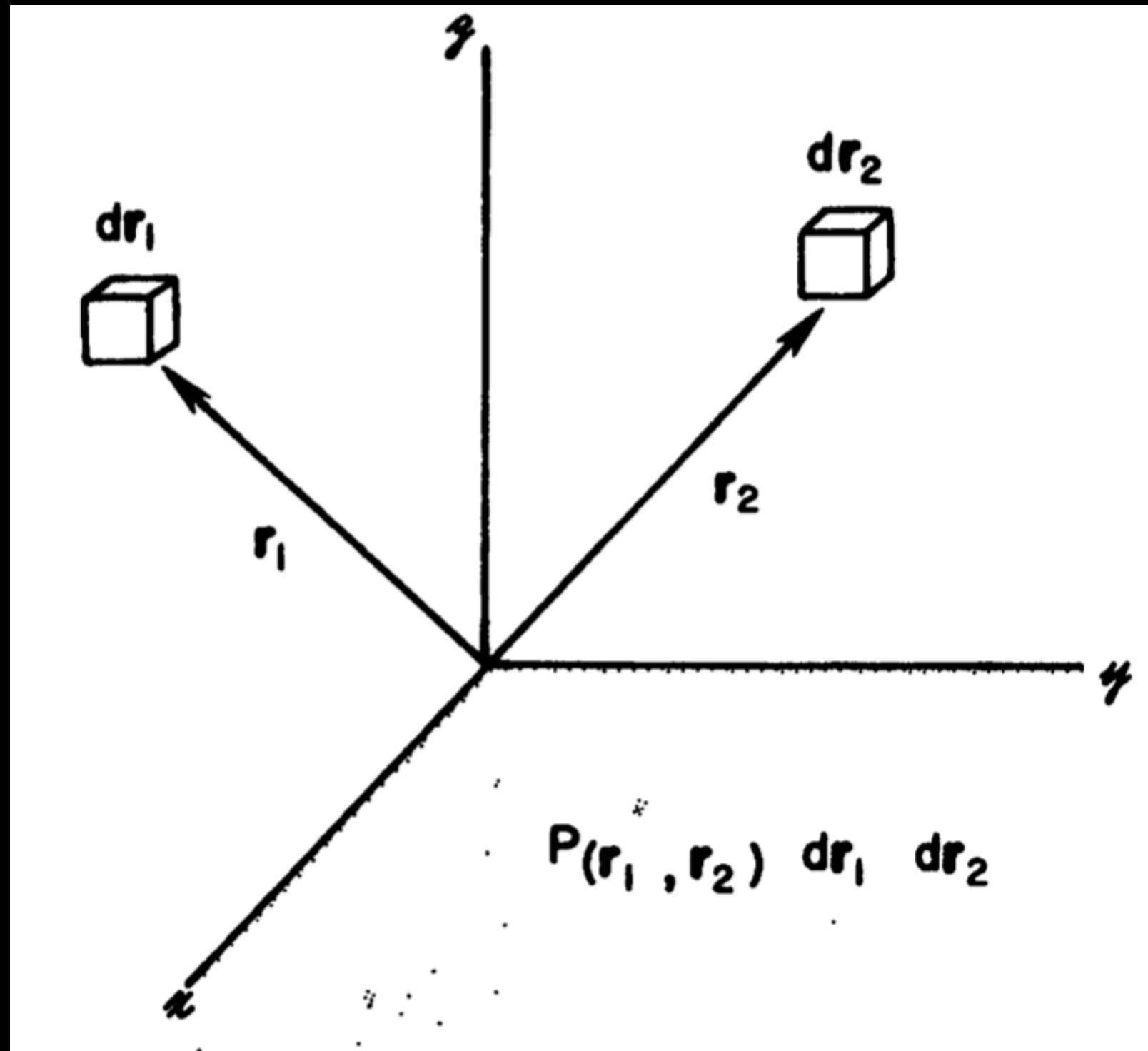
$$|\cdots\chi_m\cdots\chi_n\cdots\rangle = - |\cdots\chi_n\cdots\chi_m\cdots\rangle$$

$$|\cdots\chi_m\cdots\chi_n\cdots\rangle = \hat{a}_m^\dagger \hat{a}_n^\dagger |00\cdots 0\rangle = - \hat{a}_n^\dagger \hat{a}_m^\dagger |00\cdots 0\rangle = - |\cdots\chi_n\cdots\chi_m\cdots\rangle$$

$$\begin{array}{l} |K\rangle=|ij\rangle \\ |L\rangle=|kl\rangle \end{array}$$

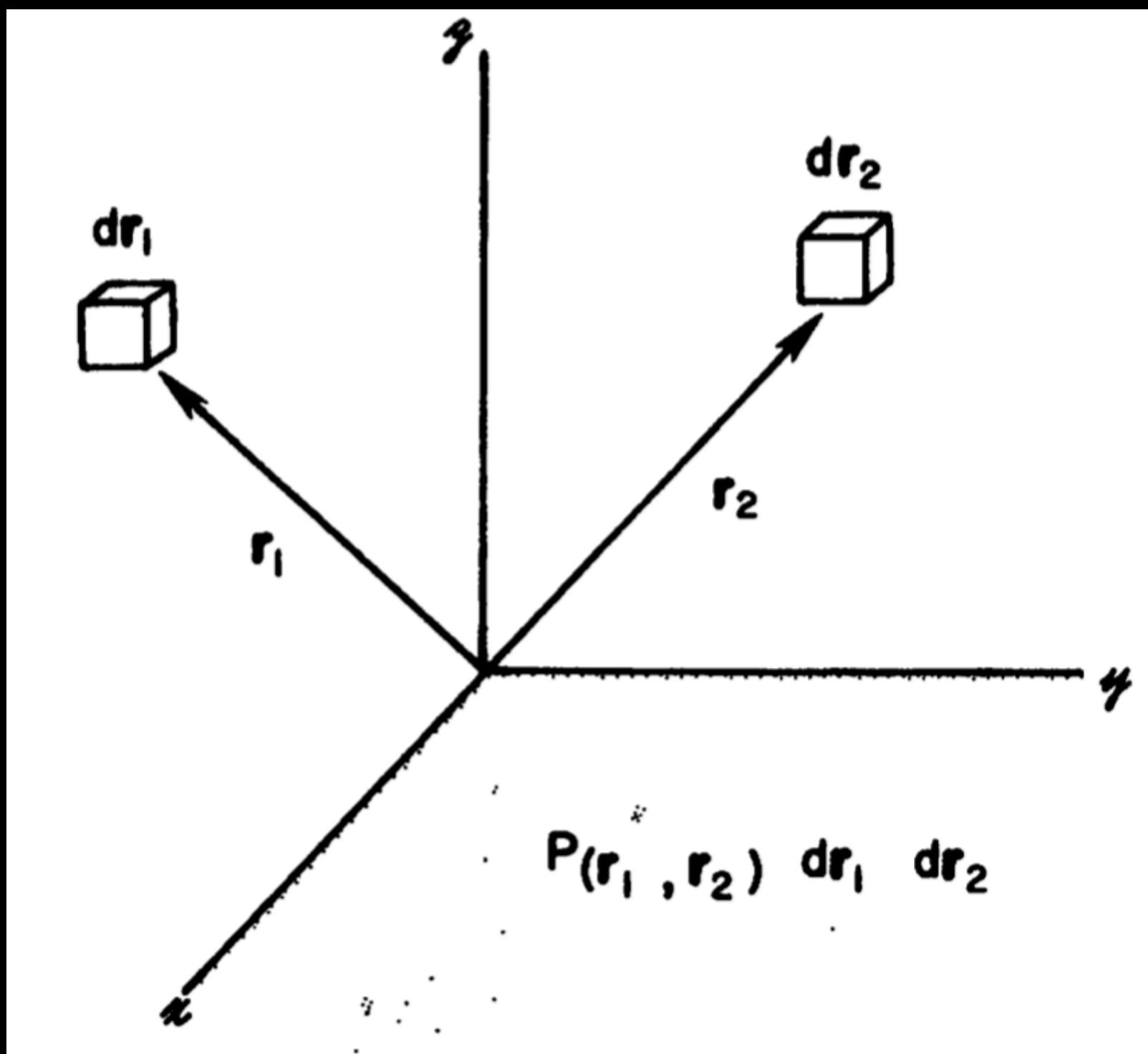
$$\begin{aligned}\langle K|L\rangle &= \frac{1}{\sqrt{2!}}\frac{1}{\sqrt{2!}}(\langle ij|-\langle ji|)(|kl\rangle-|lk\rangle) \\ &= \frac{1}{2}(\delta_{ik}\delta_{jl}-\delta_{il}\delta_{jk}-\delta_{jk}\delta_{il}+\delta_{jl}\delta_{ik}) \\ &= \delta_{ik}\delta_{jl}-\delta_{il}\delta_{jk}\end{aligned}$$

$$\begin{aligned}
|\Psi\rangle &= |12\rangle \\
&= |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\rangle \\
&= |\psi_1(\mathbf{r}_1)\sigma(\omega_1)\psi_2(\mathbf{r}_2)\sigma(\omega_2)\rangle \\
&= \hat{a}_1^\dagger \hat{a}_2^\dagger |0\rangle
\end{aligned}$$



$$\langle 12 | 12 \rangle = \iiint \psi_1^*(\mathbf{r}_1)\sigma_1^*(\omega_1)\psi_2^*(\mathbf{r}_2)\sigma_2^*(\omega_2) \times \psi_1(\mathbf{r}_1)\sigma_1(\omega_1)\psi_2(\mathbf{r}_2)\sigma_2(\omega_2) d^3r_1 d^3r_2 d\omega_1 d\omega_2$$

$$\begin{aligned}
|\Psi\rangle &= |12\rangle \\
&= |\chi_1(x_1)\chi_2(x_2)\rangle \\
&= |\psi_1(\mathbf{r}_1)\sigma(\omega_1)\psi_2(\mathbf{r}_2)\sigma(\omega_2)\rangle \\
&= \hat{a}_1^\dagger \hat{a}_2^\dagger
\end{aligned}$$



Suppose:

$$\sigma_1(\omega) = \alpha(\omega), \sigma_2(\omega) = \beta(\omega)$$

$$\langle \Psi | \Psi \rangle = \langle 12 | 12 \rangle$$

$$= \frac{1}{2}(\langle 12 | - \langle 21 |)(| 12 \rangle - | 21 \rangle)$$

$$= \frac{1}{2}(1 - 0 - 0 + 1) = 1$$

$$\begin{aligned}
\langle 12 | 12 \rangle &= \iiint \psi_1^*(\mathbf{r}_1)\sigma_1^*(\omega_1)\psi_2^*(\mathbf{r}_2)\sigma_2^*(\omega_2) \times \\
&\quad \psi_1(\mathbf{r}_1)\sigma_1(\omega_1)\psi_2(\mathbf{r}_2)\sigma_2(\omega_2) d^3r_1 d^3r_2 d\omega_1 d\omega_2
\end{aligned}$$

$$\langle \Psi | \Psi \rangle = \langle 12 | 12 \rangle$$

If use **Wick's theorem**, the deduction can become easier.

$$= \frac{1}{2} (\langle 12 | - \langle 21 |) (\langle 12 \rangle - \langle 21 \rangle)$$

$$= \frac{1}{2} \langle 0 | (\hat{a}_2 \hat{a}_1 - \hat{a}_1 \hat{a}_2) (\hat{a}_1^\dagger \hat{a}_2^\dagger - \hat{a}_2^\dagger \hat{a}_1^\dagger) | 0 \rangle$$

$$= \frac{1}{2} \langle 0 | (\hat{a}_2 \hat{a}_1 \hat{a}_1^\dagger \hat{a}_2^\dagger - \hat{a}_2 \hat{a}_1 \hat{a}_2^\dagger \hat{a}_1^\dagger -$$

$$\hat{a}_1 \hat{a}_2 \hat{a}_1^\dagger \hat{a}_2^\dagger + \hat{a}_1 \hat{a}_2 \hat{a}_2^\dagger \hat{a}_1^\dagger) | 0 \rangle$$

$$= \frac{1}{2} \times 2 = 1$$

A wide-angle photograph of a mountainous landscape. The foreground is dominated by dark, rocky terrain with patches of bright green moss or lichen. A winding dirt road cuts through the center of the frame. In the background, several peaks rise against a sky filled with soft, grey clouds. The lighting suggests either early morning or late afternoon, casting long shadows and highlighting the textures of the mountains.

# Second Quantization Representation

Another notation formula saving life

$$\left\{ \hat{a}_\alpha^\dagger, \hat{a}_\beta^\dagger \right\} \equiv \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger + \hat{a}_\beta^\dagger \hat{a}_\alpha^\dagger = 0$$

$$\left\{ \hat{a}_\alpha, \hat{a}_\beta \right\} = 0$$

$$\left\{ \hat{a}_\alpha, \hat{a}_\beta^\dagger \right\} = \delta_{\alpha\beta}$$

$$\hat{n}_i = \hat{a}_i^\dagger \hat{a}_i$$

$$\begin{aligned} & |n_1, n_2, \dots, n_i, \dots\rangle \\ &= \frac{(\hat{a}_1^\dagger)^{n_1}}{\sqrt{(n_1)!}} \frac{(\hat{a}_2^\dagger)^{n_2}}{\sqrt{(n_2)!}} \dots \frac{(\hat{a}_i^\dagger)^{n_i}}{\sqrt{(n_i)!}} \dots |0\rangle \\ &= \prod_{j=1}^N \frac{(\hat{a}_j^\dagger)^{n_j}}{\sqrt{(n_j)!}} |0\rangle \end{aligned}$$

$$\begin{aligned} & \hat{n}_i |n_1, n_2, \dots, n_i, \dots\rangle \\ &= n_i |n_1, n_2, \dots, n_i, \dots\rangle \end{aligned}$$

$$\hat{a}_i | n_1, n_2, \dots, n_i, \dots \rangle$$

$$\begin{aligned}
&= \frac{1}{\sqrt{(n_1)!(n_2)!\cdots(n_i)!\cdots}} \hat{a}_i (\hat{a}_1^\dagger)^{n_1} (\hat{a}_2^\dagger)^{n_2} \cdots (\hat{a}_i^\dagger)^{n_i} \cdots |0\rangle \\
&= \frac{(-1)^{n_1}}{\sqrt{(n_1)!(n_2)!\cdots(n_i)!\cdots}} (\hat{a}_1^\dagger)^{n_1} \hat{a}_i (\hat{a}_2^\dagger)^{n_2} \cdots (\hat{a}_i^\dagger)^{n_i} \cdots |0\rangle \\
&= \frac{(-1)^{\sum_{j=1}^{i-1} n_j}}{\sqrt{(n_1)!(n_2)!\cdots(n_i)!\cdots}} (\hat{a}_1^\dagger)^{n_1} (\hat{a}_2^\dagger)^{n_2} \cdots \hat{a}_i (\hat{a}_i^\dagger)^{n_i} \cdots |0\rangle \\
&= \frac{\sigma_i}{\sqrt{(n_1)!(n_2)!\cdots(n_i)!\cdots}} (\hat{a}_1^\dagger)^{n_1} (\hat{a}_2^\dagger)^{n_2} \cdots (1 - \hat{a}_i^\dagger \hat{a}_i) (\hat{a}_i^\dagger)^{n_i-1} \cdots |0\rangle \\
&= \sigma_i (1 - n_i) |n_1, n_2, \dots, (n_i - 1), \dots\rangle \quad \left\{ \begin{array}{ll} = 0, & n_i = 0 \\ = \sigma_i |n_1, n_2, \dots, 0_i, \dots\rangle, & n_i = 1 \end{array} \right.
\end{aligned}$$

$$\hat{a}_i^\dagger |n_1, n_2, \dots, n_i, \dots\rangle$$

$$= \frac{1}{\sqrt{(n_1)!(n_2)!\cdots(n_i)!\cdots}} \hat{a}_i^\dagger (\hat{a}_1^\dagger)^{n_1} (\hat{a}_2^\dagger)^{n_2} \cdots (\hat{a}_i^\dagger)^{n_i} \cdots |0\rangle$$

$$= \frac{(-1)^{n_1}}{\sqrt{(n_1)!(n_2)!\cdots(n_i)!\cdots}} (\hat{a}_1^\dagger)^{n_1} \hat{a}_i^\dagger (\hat{a}_2^\dagger)^{n_2} \cdots (\hat{a}_i^\dagger)^{n_i} \cdots |0\rangle$$

$$= \frac{(-1)^{\sum_{j=1}^{i-1} n_j}}{\sqrt{(n_1)!(n_2)!\cdots(n_i)!\cdots}} (\hat{a}_1^\dagger)^{n_1} (\hat{a}_2^\dagger)^{n_2} \cdots \hat{a}_i^\dagger (\hat{a}_i^\dagger)^{n_i} \cdots |0\rangle$$

$$\sigma_i = (-1)^{\sum_{j=1}^{i-1} n_j}$$

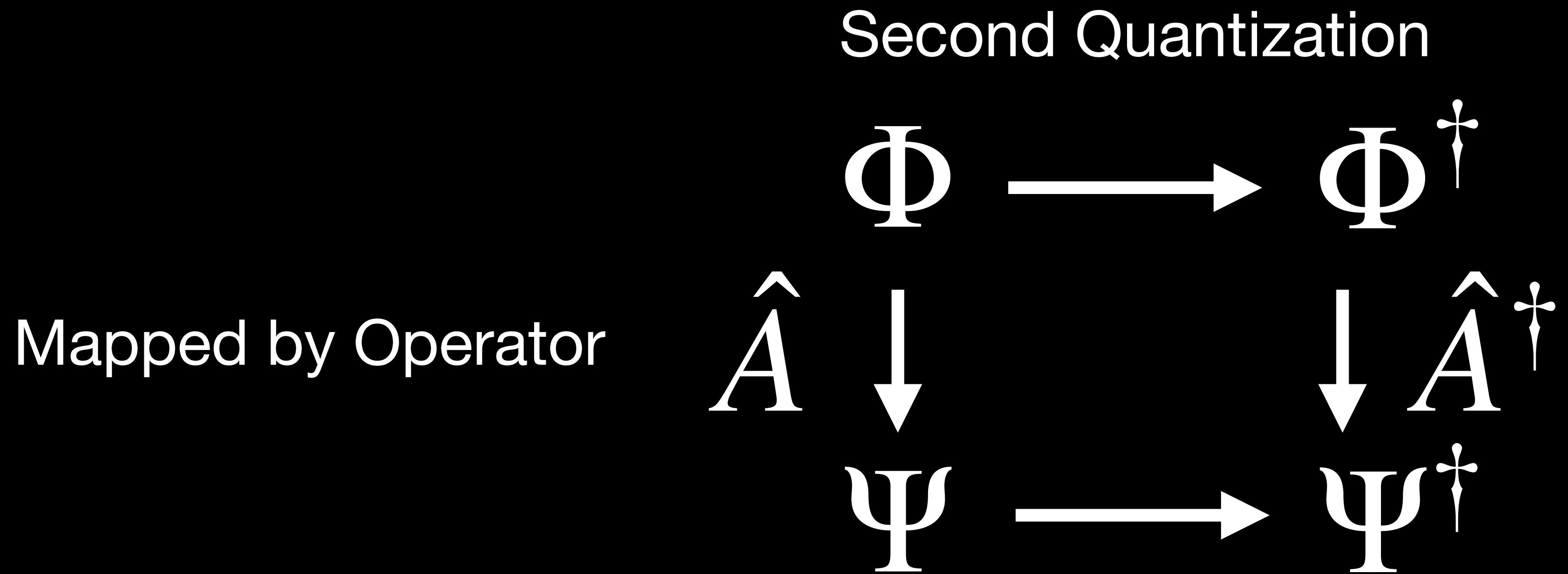
$$\hat{a}_i^\dagger |n_i\rangle = \sqrt{n_i + 1} |n_i + 1\rangle$$

$$= \sigma_i \sqrt{n_i + 1} |n_1, n_2, \dots, n_i + 1, \dots\rangle \quad \begin{cases} = \sigma_i |n_1, n_2, \dots, 1_i, \dots\rangle, & n_i = 0 \\ = 0, & n_i = 1 \end{cases}$$

$$\begin{aligned}
\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) &= (N!)^{-1/2} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \cdots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \cdots & \chi_k(\mathbf{x}_2) \\ \vdots & \vdots & \cdots & \vdots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \cdots & \chi_k(\mathbf{x}_N) \end{vmatrix} \\
&= |\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N)\rangle \\
&= |\chi_i\chi_j\cdots\chi_k\rangle = |ij\cdots k\rangle \\
&= \hat{a}_i^\dagger \hat{a}_j^\dagger \cdots \hat{a}_k^\dagger |00\cdots 0\rangle \\
&= \hat{a}_i^\dagger \hat{a}_j^\dagger \cdots \hat{a}_k^\dagger |0\rangle \quad n_i = 1
\end{aligned}$$

In ground state calculations, all the shown positions are single-occupied.  
So there is slight difference from the general case.

# Second quantization of operators



**Table 3.1** First and second quantization treatment of conserved particles.

|                               | First quantization   | Second quantization   |
|-------------------------------|--|---|
| Wavefunction → field operator | $\psi(x) = \langle x   \psi \rangle$   | $\hat{\psi}(x)$   |
| Commutator                    | $[x, p] = i\hbar$  | $[\hat{\psi}(x), \hat{\psi}^\dagger(x')]_\mp = \delta^D(x - x')$  |
| Density                       | $\rho(x) =  \psi(x) ^2$  | $\hat{\rho}(x) = \hat{\psi}^\dagger(x)\hat{\psi}(x)$  |
| Arbitrary basis               | $\psi_\lambda = \langle \lambda   \psi \rangle$  | $\hat{\psi}_\lambda$  |
| Change of basis               | $\langle \tilde{s}   \psi \rangle = \sum_\lambda \langle \tilde{s}   \lambda \rangle \langle \lambda   \psi \rangle$ | $\hat{a}_s = \sum_\lambda \langle \tilde{s}   \lambda \rangle \hat{\psi}_\lambda$   |
| Orthogonality                 | $\langle \lambda   \lambda' \rangle = \delta_{\lambda\lambda'}$  | $[\psi_\lambda, \psi_{\lambda'}^\dagger]_\mp = \delta_{\lambda\lambda'}$  |
| One-particle energy           | $\frac{p^2}{2m} + U$   | $\int_x \hat{\psi}^\dagger(x) \left( -\frac{\hbar^2}{2m} + U(x) \right) \hat{\psi}(x)$  |
| Interaction                   | $\sum_{i < j} V(x_i - x_j)$  | $\hat{V} = \frac{1}{2} \int_{x,x'} V(x - x') : \hat{\rho}(x) \hat{\rho}(x') : = \frac{1}{2} \sum V(\mathbf{q}) c_{\mathbf{k}+\mathbf{q}}^\dagger c_{\mathbf{k}'-\mathbf{q}}^\dagger c_{\mathbf{k}'} c_{\mathbf{k}}$ |
| Many-body wavefunction        | $\Psi(x_1, x_2, \dots, x_N)$   | $\langle 0   \hat{\psi}(x_1) \cdots \hat{\psi}(x_N)   \Psi \rangle$   |
| Schrödinger equation          | $\left( \sum \mathcal{H}_i + \sum_{i < j} V_{ij} \right) \Psi = i\hbar \dot{\Psi}$                                   | $[\mathcal{H}^{(0)} + \int_{x'} \hat{\rho}(x') V(x' - x)] \hat{\psi}(x) = i\hbar \dot{\psi}(x)$   |

# Single-particle operator

First, we consider single electron case.

$$\hat{A}\phi_i = \psi_i$$

$$\psi_i = \sum_k C_{ik} \phi_k$$

$$\hat{A}\phi_i = \sum_k C_{ik} \phi_k$$

$$\langle \phi_l | \hat{A} | \phi_i \rangle = \sum_k C_{ik} \langle \phi_l | \phi_k \rangle$$

$$A_{li} = C_{il}$$

$$\hat{A}^\dagger \phi_i^\dagger |0\rangle = \psi_i^\dagger |0\rangle$$

Second quantization:

$$\psi_i^\dagger = \sum_k C_{ik} \phi_k^\dagger$$

$$\hat{A}^\dagger \phi_i^\dagger = \sum_k C_{ik} \phi_k^\dagger$$

$$\hat{A}^\dagger \phi_i^\dagger \phi_i = \sum_k C_{ik} \phi_k^\dagger \phi_i$$

$$\hat{A}^\dagger \sum_i \phi_i^\dagger \phi_i = \sum_{k,i} C_{ik} \phi_k^\dagger \phi_i$$

$$\hat{A}^\dagger \hat{N} = \sum_{k,i} C_{ik} \phi_k^\dagger \phi_i$$

Since there is  
only 1 electron

$$\hat{A}^\dagger = \sum_{k,i} C_{ik} \phi_k^\dagger \phi_i$$

Insert the relation:  $A_{li} = C_{il}$

$$\hat{A}^\dagger = \sum_{k,i} A_{ki} \phi_k^\dagger \phi_i$$

$$\hat{A} \longrightarrow \sum_{k,i} A_{ki} \phi_k^\dagger \phi_i$$

# Proof of the second quantization of single electron operator

$$\langle \phi_l | \hat{A} | \phi_l \rangle = A_{ll}$$

$$\langle \phi_l | \sum_{k,i} A_{ki} \phi_k^\dagger \phi_i | \phi_l \rangle$$

$$= \langle 0 | \phi_l \sum_{k,i} A_{ki} \phi_k^\dagger \phi_i \phi_l^\dagger | 0 \rangle = \langle 0 | \sum_{k,i} A_{ki} \phi_l \phi_k^\dagger \phi_i \phi_l^\dagger | 0 \rangle$$

$$= \langle 0 | \sum_{k,i} A_{ki} (\delta_{lk} - \phi_k^\dagger \phi_l) (\delta_{il} - \phi_l^\dagger \phi_i) | 0 \rangle$$

$$= \langle 0 | \sum_{k,i} A_{ki} \delta_{lk} (\delta_{il} - \phi_l^\dagger \phi_i) + \phi_k^\dagger \phi_i (1 - \hat{n}_l) | 0 \rangle$$

$$= \langle 0 | \sum_{k,i} A_{ki} \delta_{lk} \delta_{il} | 0 \rangle = \textcircled{A_{ll}}$$

# Extend our finding to $N$ -particles

This single-particle operator has lots of examples, such as:

$$\hat{A} = \sum_{n=1}^N \hat{A}_n \quad \hat{T} = -\frac{1}{2} \sum_n \nabla_n^2 \quad \hat{V} = -\sum_n \left[ \sum_A \frac{z_A}{|R_A - r_n|} \right] \quad \hat{\mu} = \sum_n \hat{\mu}_n$$

$$\Psi = \hat{A}\Phi \longrightarrow \Psi^\dagger = \hat{A}^\dagger\Phi^\dagger$$

$$\begin{aligned} \Psi^\dagger |0\rangle &= \sum_n \hat{A}_n^\dagger \Phi_n^\dagger |0\rangle \\ &= \sum_n \hat{A}_n^\dagger \phi_N^\dagger \cdots \phi_n^\dagger \cdots \phi_1^\dagger |0\rangle \\ \hat{A}_n^\dagger \phi_n^\dagger &= \sum_l C_{nl} \phi_l^\dagger \\ &= \sum_l A_{ln} \phi_l^\dagger \end{aligned}$$

$$\Psi^\dagger |0\rangle = \sum_n \phi_1^\dagger \cdots (\sum_l C_{nl} \phi_l^\dagger) \cdots \phi_N^\dagger |0\rangle$$

$$\hat{A}_n^\dagger \phi_n^\dagger = \sum_l A_{ln} \phi_l^\dagger$$

$$= \sum_n \sum_l A_{ln} \phi_1^\dagger \cdots \phi_l^\dagger \cdots \phi_N^\dagger |0\rangle$$

$$A_{ln} = \langle l | \hat{A} | n \rangle$$

$$= \sum_{n,l} A_{ln} \phi_1^\dagger \cdots \phi_l^\dagger (\phi_n \phi_n^\dagger) \cdots \phi_N^\dagger |0\rangle$$

$$= \sum_{n,l} A_{ln} (-1)^{l-1} \phi_l^\dagger (-1)^{l-1} \phi_n \phi_1^\dagger \cdots \phi_n^\dagger \cdots \phi_N^\dagger |0\rangle$$

$$= \sum_{n,l} (A_{ln} \phi_l^\dagger \phi_n) \left[ \phi_1^\dagger \cdots \phi_n^\dagger \cdots \phi_N^\dagger |0\rangle \right]$$

$$\hat{A}_{\text{(single-particle)}} \rightarrow \sum_{n,l} A_{ln} \phi_l^\dagger \phi_n$$

# Verification of the one-body operator

$$|\Psi_0\rangle = |1\cdots a \cdots b \cdots N\rangle$$

$$\langle\Psi_0|\hat{O}_1|\Psi_0\rangle = \sum_{\mu\nu} \langle\mu|\hat{h}|\nu\rangle \langle\Psi_0|\hat{a}_\mu^\dagger \hat{a}_\nu|\Psi_0\rangle$$

Here we are considering the ground state, so  $\mu$  and  $\nu$  must be within the set  $\{1, 2, \dots, a, \dots, b, \dots, N\}$ :

$$\begin{aligned}\langle\Psi_0|\hat{O}_1|\Psi_0\rangle &= \sum_{ab} \langle a|\hat{h}|b\rangle \langle\Psi_0|\hat{a}_a^\dagger \hat{a}_b|\Psi_0\rangle \\ &= \sum_{ab} \langle a|\hat{h}|b\rangle \langle\Psi_0|(\delta_{ab} - \hat{a}_b \hat{a}_a^\dagger)|\Psi_0\rangle\end{aligned}$$

Since in the ground state, all  $\{1, \dots, a, \dots, b, \dots, N\}$  are occupied, add a new one cause the Slater determinant being zero, we have:

$$\langle\Psi_0|\hat{O}_1|\Psi_0\rangle = \sum_{ab} \langle a|\hat{h}|b\rangle \langle\Psi_0|(\delta_{ab})|\Psi_0\rangle = \sum_a \langle a|\hat{h}|a\rangle$$

# Double-particle operator

$$\begin{aligned}
\hat{A} &= \sum_{i<j}^N \hat{A}_{ij} \xrightarrow{\text{S.Q.}} \sum_{i<j}^N \hat{A}_{ij}^\dagger = \sum_{i<j}^N \hat{A}_{ij}^\dagger \phi_1^\dagger \cdots \phi_i^\dagger \cdots \phi_j^\dagger \cdots \phi_N^\dagger |0\rangle \\
&= \sum_{i<j}^N \phi_1^\dagger \cdots \psi_i^\dagger \cdots \psi_j^\dagger \cdots \phi_N^\dagger |0\rangle \\
&= \sum_{i<j}^N \sum_{k,l} C_{ij,kl} \phi_1^\dagger \cdots \phi_k^\dagger \cdots \phi_l^\dagger \cdots \phi_N^\dagger |0\rangle
\end{aligned}$$

From quantum mechanics of first quantization, we have known:

$$C_{ij,kl} = \int \int d^3r d^3r' \phi_k(\mathbf{r}) \phi_l(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') = \langle kl | ij \rangle$$

And we suppose  $\sum_{i<j}^N \hat{A}_{ij}^\dagger$  has the expansion:  $\sum_{i<j}^N \hat{A}_{ij}^\dagger = \sum_{i<j}^N \sum_{k,l} A_{ij,kl} \phi_k^\dagger \phi_l^\dagger \phi_i \phi_j$

Now let us try to find the relationship between  $A_{ij,kl}$  and  $C_{ij,kl}$ .

$$\begin{aligned}
& \sum_{i < j}^N \sum_{k,l} (A_{ij,kl} \phi_k^\dagger \phi_l^\dagger \phi_i \phi_j) \phi_1^\dagger \cdots \phi_i^\dagger \cdots \phi_j^\dagger \cdots \phi_N^\dagger |0\rangle \\
&= \sum_{i < j}^N \sum_{k,l} (A_{ij,kl} \phi_k^\dagger \phi_l^\dagger) (-1)^{i-1} (-1)^{j-1} \phi_1^\dagger \cdots \phi_{i-1}^\dagger \phi_{i+1}^\dagger \cdots \phi_{j-1}^\dagger \phi_{j+1}^\dagger \cdots \phi_N^\dagger |0\rangle \\
&= \sum_{i < j}^N \sum_{k,l} (A_{ij,kl} \phi_k^\dagger) (-1)^{j-2} (-1)^{i-1} (-1)^{j-1} \phi_1^\dagger \cdots \phi_{i-1}^\dagger \phi_{i+1}^\dagger \cdots \phi_{j-1}^\dagger \phi_l^\dagger \phi_{j+1}^\dagger \cdots \phi_N^\dagger |0\rangle \\
&= \sum_{i < j}^N \sum_{k,l} A_{ij,kl} (-1)^{(i-1)+(j-2)+(i-1)+(j-1)} [\phi_1^\dagger \cdots \phi_i^\dagger \cdots \phi_j^\dagger \cdots \phi_N^\dagger |0\rangle] \\
&= \sum_{i < j}^N \sum_{k,l} (-A_{ij,kl}) [\phi_1^\dagger \cdots \phi_i^\dagger \cdots \phi_j^\dagger \cdots \phi_N^\dagger |0\rangle]
\end{aligned}$$

$$A_{ij,kl} = -C_{ij,kl}$$

Example of the sign changing:

$$\begin{aligned}& \phi_3^\dagger \phi_5^\dagger \phi_3 \phi_5 |1,2,3,4,5,6\rangle \\&= (-1)^4 \phi_3^\dagger \phi_5^\dagger \phi_3 |1,2,3,4,\times,6\rangle \\&= (-1)^4 (-1)^2 \phi_3^\dagger \phi_5^\dagger |1,2,\times,4,\times,6\rangle \\&= (-1)^4 (-1)^2 (-1)^3 \phi_3^\dagger |1,2,\times,4,5,6\rangle \\&= (-1)^4 (-1)^2 (-1)^3 (-1)^2 |1,2,3,4,5,6\rangle \\&= -|1,2,3,4,5,6\rangle\end{aligned}$$

Since when  $i = j$ , there would be two same annihilation operators:

$$\hat{A}_{ii}^\dagger = \sum_{k,l} A_{ii,kl} \phi_k^\dagger \phi_l^\dagger \phi_i \phi_i = \hat{0}$$

For fermion that is equal to zero, so we can remove the constraint  $i < j$ , and make the summation run over all the possibilities, and then divide by two.

$$\hat{A}_{\text{(two-particle)}}^\dagger = \sum_{i < j}^N \hat{A}_{ij}^\dagger = -\frac{1}{2} \sum_{ijkl} C_{ij,kl} \phi_k^\dagger \phi_l^\dagger \phi_i \phi_j = -\frac{1}{2} \sum_{ijkl} \langle kl | ij \rangle \phi_k^\dagger \phi_l^\dagger \phi_i \phi_j$$

At last, we can use a trick to remove the minus sign using anti-commutation relation.

$$\hat{A}_{\text{(two-particle)}}^\dagger = \sum_{i < j}^N \hat{A}_{ij}^\dagger = \frac{1}{2} \sum_{ijkl} \langle kl | ij \rangle \phi_k^\dagger \phi_l^\dagger \phi_{\textcolor{red}{j}} \phi_{\textcolor{red}{i}}$$

# B-O Hamiltonian from Second quantization

Collect all the expressions

$$\begin{aligned}\hat{H} &= \sum_i \hat{h}_i + \sum_{i < j} \frac{1}{r_{ij}} \\ &= \sum_{\mu\nu} h_{\mu\nu} \hat{a}_{\mu}^{\dagger} \hat{a}_{\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \langle \mu\nu | \lambda\sigma \rangle \hat{a}_{\mu}^{\dagger} \hat{a}_{\nu}^{\dagger} \hat{a}_{\sigma} \hat{a}_{\lambda}\end{aligned}$$

$$\sum_i \hat{h}_i = \sum_{ij} h_{ij} \hat{a}_i^{\dagger} \hat{a}_j = \sum_{ij} h_{ij} (\delta_{ij} - \hat{a}_j \hat{a}_i^{\dagger})$$

When considering ground state Slater determinant, since in it all possible  $i$ -positions are occupied, so that when create an electron at the  $i^{\text{th}}$  position, the determinant would be zero.

$$\hat{H} = \sum_i h_{ii} \hat{a}_i^{\dagger} \hat{a}_i + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \langle \mu\nu | \lambda\sigma \rangle \hat{a}_{\mu}^{\dagger} \hat{a}_{\nu}^{\dagger} \hat{a}_{\sigma} \hat{a}_{\lambda}$$

# Verification of the two-body operator

$$|\Psi_0\rangle = |1\cdots a \cdots b \cdots N\rangle$$

$$\langle\Psi_0|\hat{O}_2|\Psi_0\rangle = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \langle\mu\nu|\lambda\sigma\rangle \langle\Psi_0|\hat{a}_\mu^\dagger \hat{a}_\nu^\dagger \hat{a}_\sigma \hat{a}_\lambda|\Psi_0\rangle$$

Here we are considering the ground state,  
so  $\mu$  and  $\nu$  must be within the set  
 $\{1, 2, \dots, a, \dots, b, \dots, N\}$ :

$$\langle\Psi_0|\hat{O}_2|\Psi_0\rangle = \frac{1}{2} \sum_{abcd} \langle ab|cd\rangle \langle\Psi_0|\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_d \hat{a}_c|\Psi_0\rangle$$

$$\begin{aligned}
\langle \Psi_0 | \hat{O}_2 | \Psi_0 \rangle &= \frac{1}{2} \sum_{ab} \langle ab | cd \rangle \langle \Psi_0 | \hat{a}_a^\dagger (\delta_{bd} - \hat{a}_d \hat{a}_b^\dagger) \hat{a}_c | \Psi_0 \rangle \\
&= \frac{1}{2} \sum_{ab} \langle ab | cd \rangle \langle \Psi_0 | \delta_{bd} \hat{a}_a^\dagger \hat{a}_c - \hat{a}_a^\dagger \hat{a}_d \hat{a}_b^\dagger \hat{a}_c | \Psi_0 \rangle \\
&= \frac{1}{2} \sum_{ab} \langle ab | cd \rangle \langle \Psi_0 | \delta_{bd} (\delta_{ac} - \hat{a}_c \hat{a}_a^\dagger) - \hat{a}_a^\dagger \hat{a}_d (\delta_{bc} - \hat{a}_c \hat{a}_b^\dagger) | \Psi_0 \rangle \\
&= \frac{1}{2} \sum_{ab} \langle ab | cd \rangle \langle \Psi_0 | \delta_{bd} \delta_{ac} - \cancel{\delta_{ba} \hat{a}_c \hat{a}_a^\dagger} - \hat{a}_a^\dagger \hat{a}_d \delta_{bc} + \cancel{\hat{a}_c^\dagger \hat{a}_d \hat{a}_c \hat{a}_b^\dagger} | \Psi_0 \rangle \\
&= \frac{1}{2} \sum_{ab} \langle ab | cd \rangle \langle \Psi_0 | \delta_{bd} \delta_{ac} - \delta_{bc} (\delta_{ad} - \cancel{\hat{a}_d \hat{a}_a^\dagger}) | \Psi_0 \rangle \\
&= \frac{1}{2} \sum_{ab} [\langle ab | ab \rangle - \langle ab | ba \rangle]
\end{aligned}$$

**Back to main text**



Suppose:

$$\sigma_1(\omega) = \beta(\omega), \sigma_2(\omega) = \beta(\omega)$$

$$\langle \Psi | \Psi \rangle = \langle 12 | 21 \rangle$$

$$= \frac{1}{2} (\langle 12 | - \langle 21 |)(| 12 \rangle - | 21 \rangle)$$

$$= \frac{1}{2} (1 - S - S + 1) = 1 - S$$

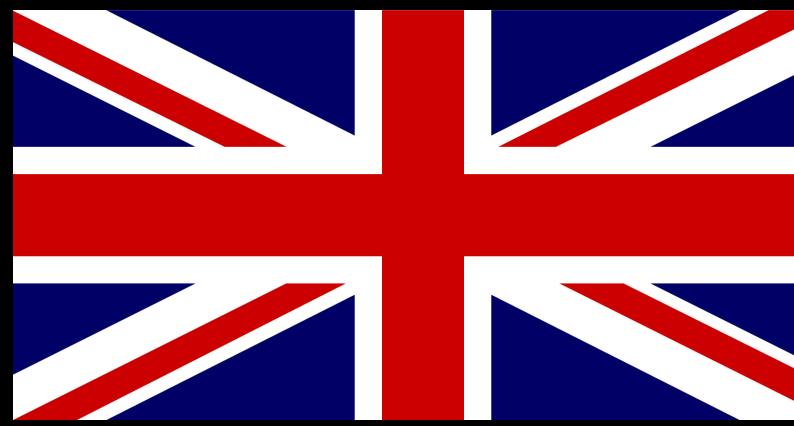
$$\langle 12 | 21 \rangle = \iint \psi_1^*(\mathbf{r}_1) \beta_1^*(\omega_1) \psi_2^*(\mathbf{r}_2) \beta_2^*(\omega_2) \times$$

$$\psi_2(\mathbf{r}_1) \beta_2(\omega_1) \psi_1(\mathbf{r}_2) \beta_1(\omega_2) d^3 r_1 d^3 r_2$$

**Fermi hole**

$$= \iint \psi_1^*(\mathbf{r}_1) \psi_2^*(\mathbf{r}_2) \psi_2(\mathbf{r}_1) \psi_1(\mathbf{r}_2) d^3 r_1 d^3 r_2 = S$$

# Hartree-Fock approximation



<https://mathshistory.st-andrews.ac.uk/Biographies/Hartree/>

<https://physicstoday.scitation.org/do/10.1063/pt.6.6.20171222a/full/>

$$|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_N\rangle$$

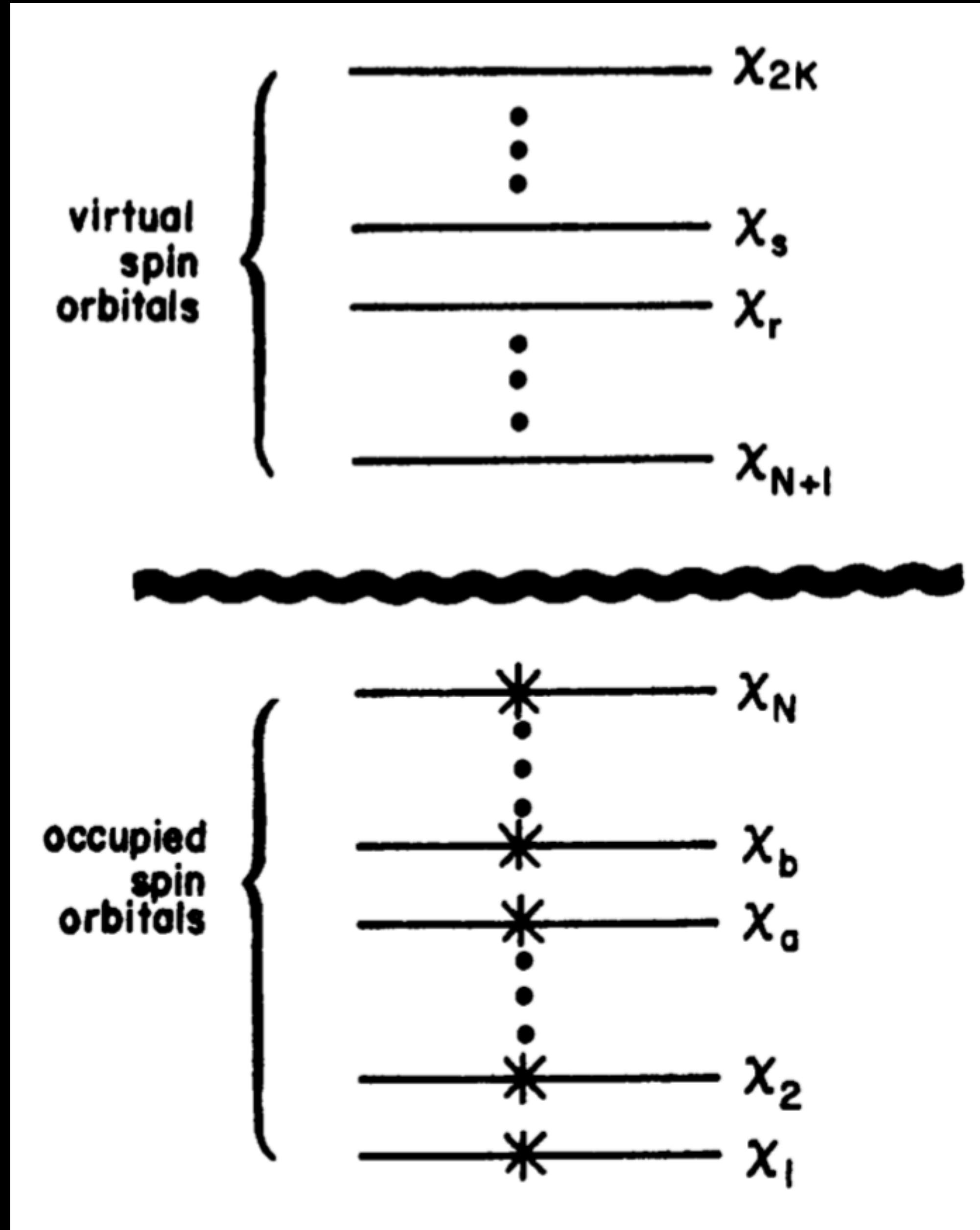
From variation principle, the best wave function of this functional form is the one which gives the lowest possible energy

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

Once one can **optimize** the wave function, one can obtain the best estimation from Hartree-Fock method.

$$\hat{f}(i)\chi(x_i) = \varepsilon\chi(x_i)$$

$$\hat{f}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v^{\text{HF}}(i)$$



## The Hartree-Fock ground state

$$|\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle$$

# Minimal basis model

First, consider the atomic orbital:

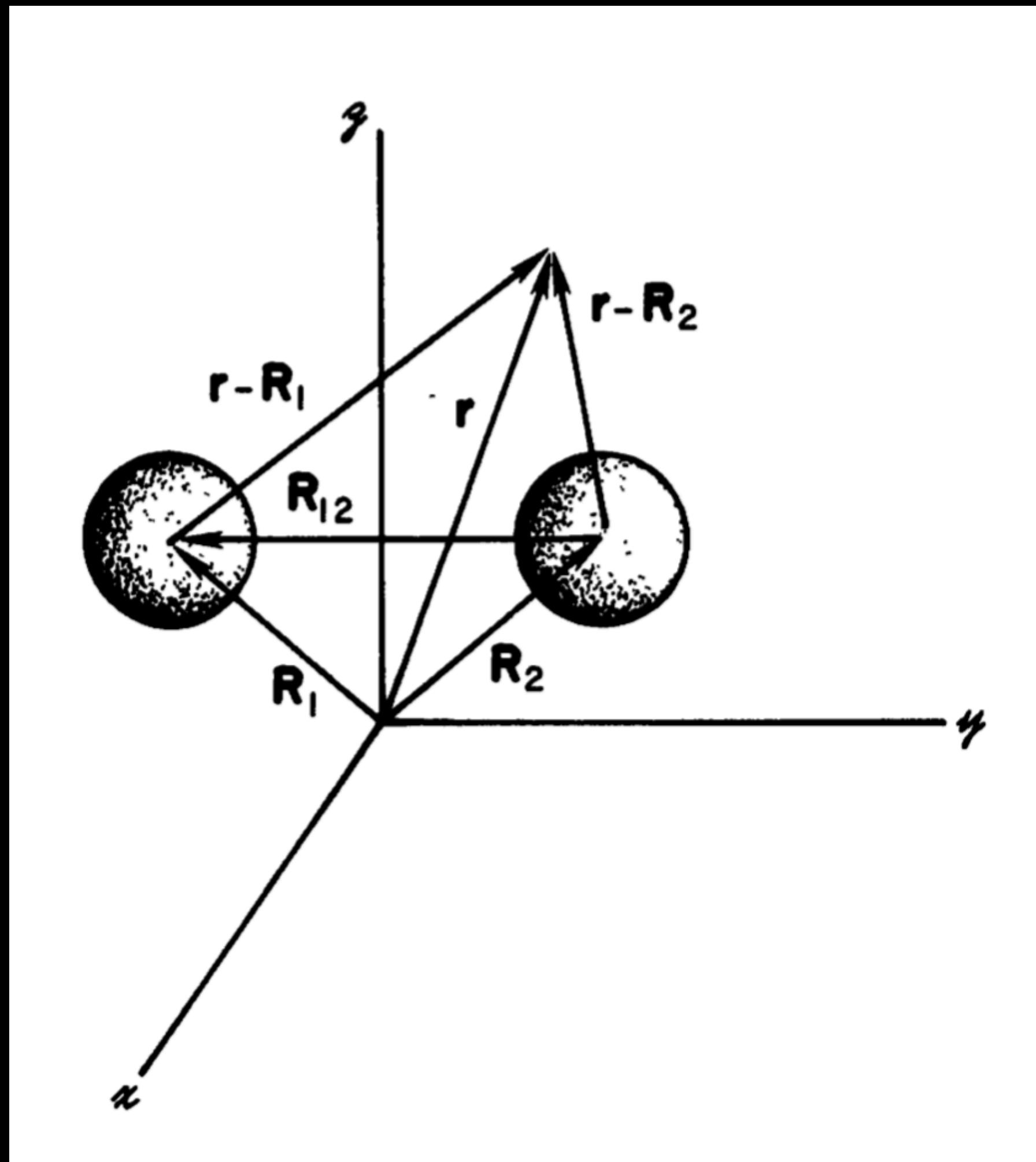
$$\phi_1 \equiv \phi_1(\mathbf{r} - \mathbf{R}_1) \quad \phi_2 \equiv \phi_2(\mathbf{r} - \mathbf{R}_2)$$

Slater orbital:  $\phi(\mathbf{r} - \mathbf{R}) = \left(\frac{\zeta^3}{\pi}\right)^{1/2} e^{-\zeta|\mathbf{r}-\mathbf{R}|}$

Gauss orbital:

$$\phi(\mathbf{r} - \mathbf{R}) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha|\mathbf{r}-\mathbf{R}|^2}$$

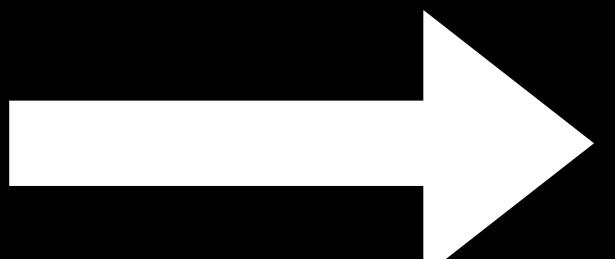
$$\langle \phi_1 | \phi_2 \rangle = S$$



# LCAO from the minimal basis

$$\psi_1 = [2(1 + S)]^{-1/2}(\phi_1 + \phi_2)$$

$$\psi_2 = [2(1 + S)]^{-1/2}(\phi_1 - \phi_2)$$



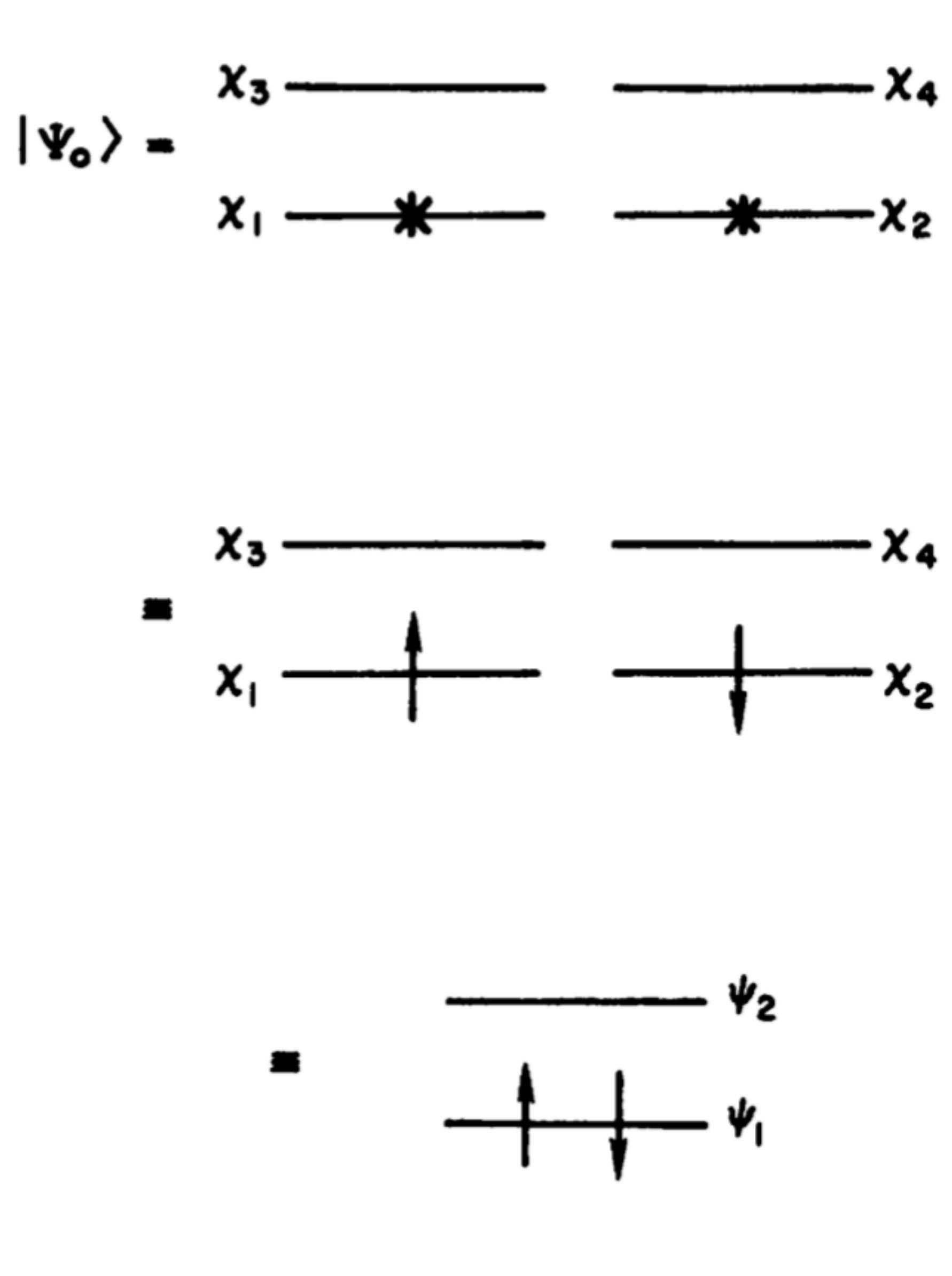
$$\chi_1 = \psi_1(\mathbf{r})\alpha(\omega)$$

$$\chi_2 = \psi_1(\mathbf{r})\beta(\omega)$$

$$\chi_3 = \psi_2(\mathbf{r})\alpha(\omega)$$

$$\chi_4 = \psi_2(\mathbf{r})\beta(\omega)$$

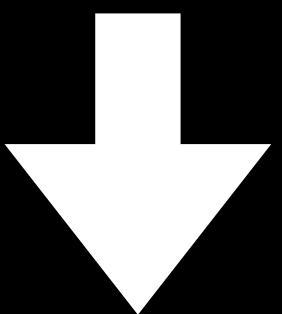
$$|\Psi_0\rangle = |\chi_1\chi_2\rangle$$



$$|\Psi_0\rangle = |\chi_1\chi_2\rangle$$

$$\chi_1 \equiv \psi_1, \quad \chi_2 \equiv \bar{\psi}_1$$

$$\chi_3 \equiv \psi_2, \quad \chi_4 \equiv \bar{\psi}_2$$

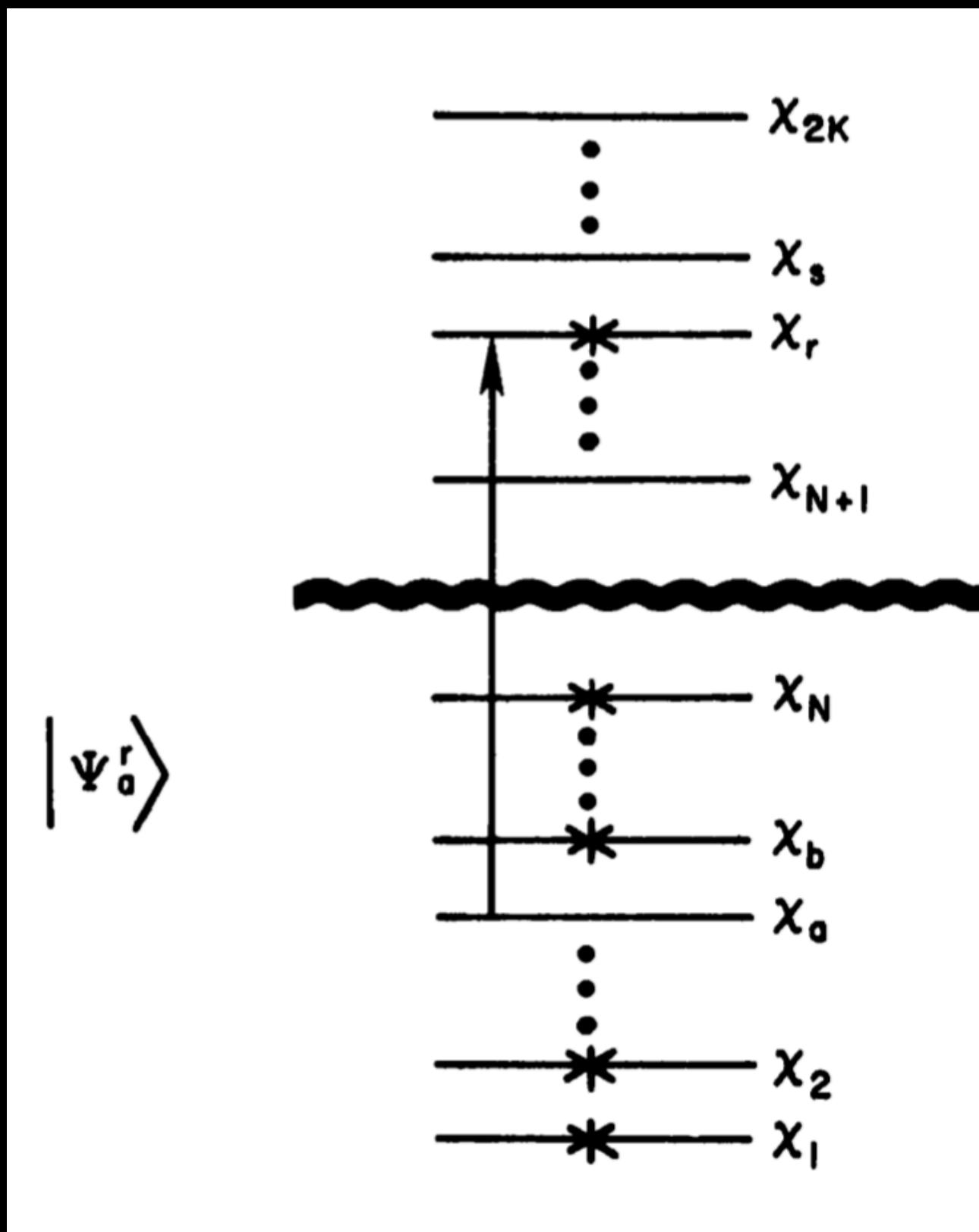


$$|\Psi_0\rangle = |\psi_1\bar{\psi}_1\rangle$$

# Excited Determinants

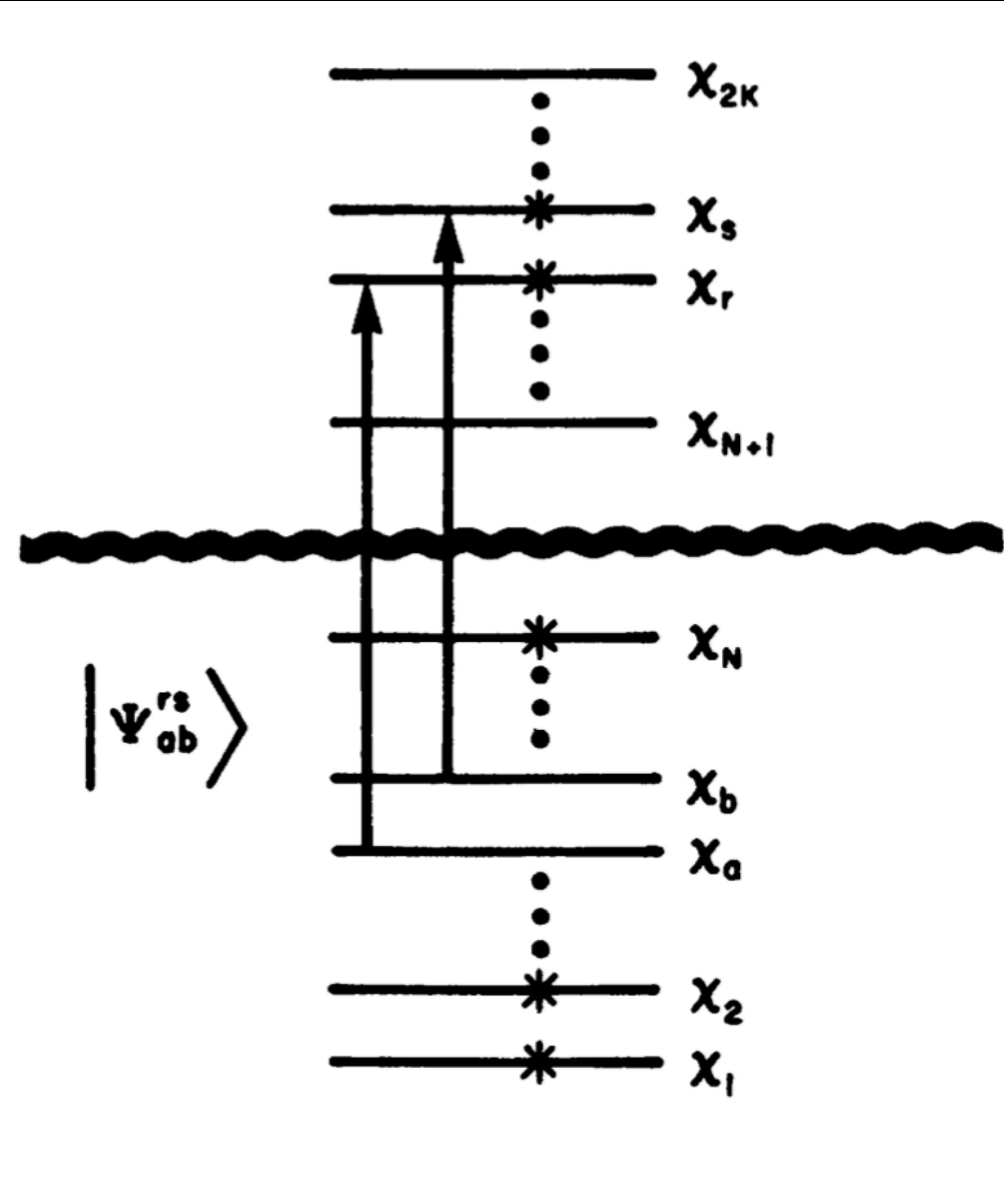
$$|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle$$

With  $2K$  orbitals and  $N$  electrons, there are multiple different Slater determinants:



$$\binom{2K}{N} = \frac{(2K)!}{N!(2K - N)!}$$

After H-F calculation, the energy of each  $\chi_i$  is fixed. So the choices different from the ground state Slater determinant can be explained as excitation.



$$|\Psi_a^r\rangle = |\chi_1 \chi_2 \cdots \chi_r \chi_b \cdots \chi_N\rangle$$

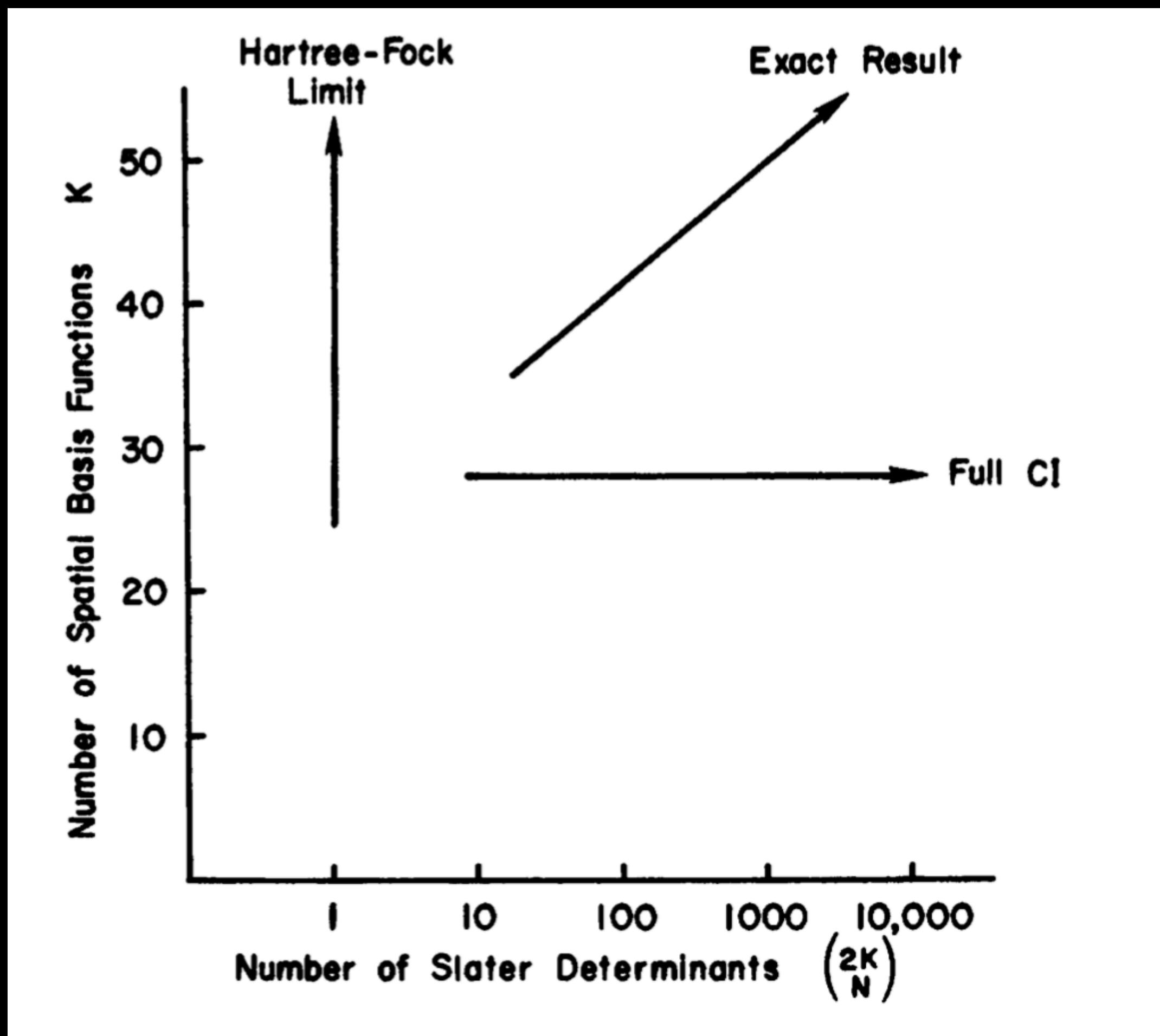
$$|\Psi_{ab}^{rs}\rangle = |\chi_1 \chi_2 \cdots \chi_r \chi_s \cdots \chi_N\rangle$$

$$|\Phi\rangle = c_0 |\Psi_0\rangle + \sum_{ra} c_a^r |\Psi_a^r\rangle + \sum_{a < b, r < s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \dots$$

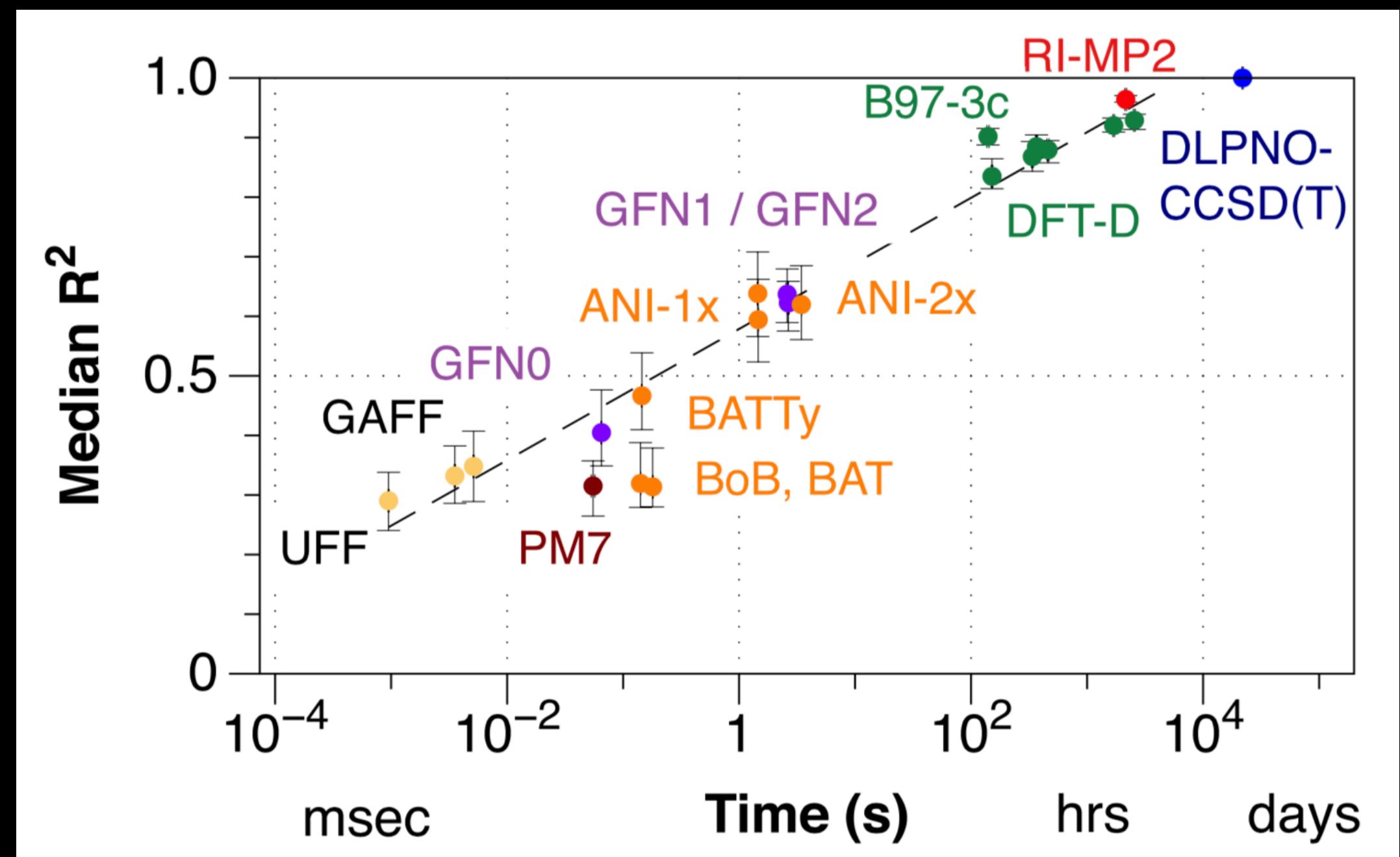
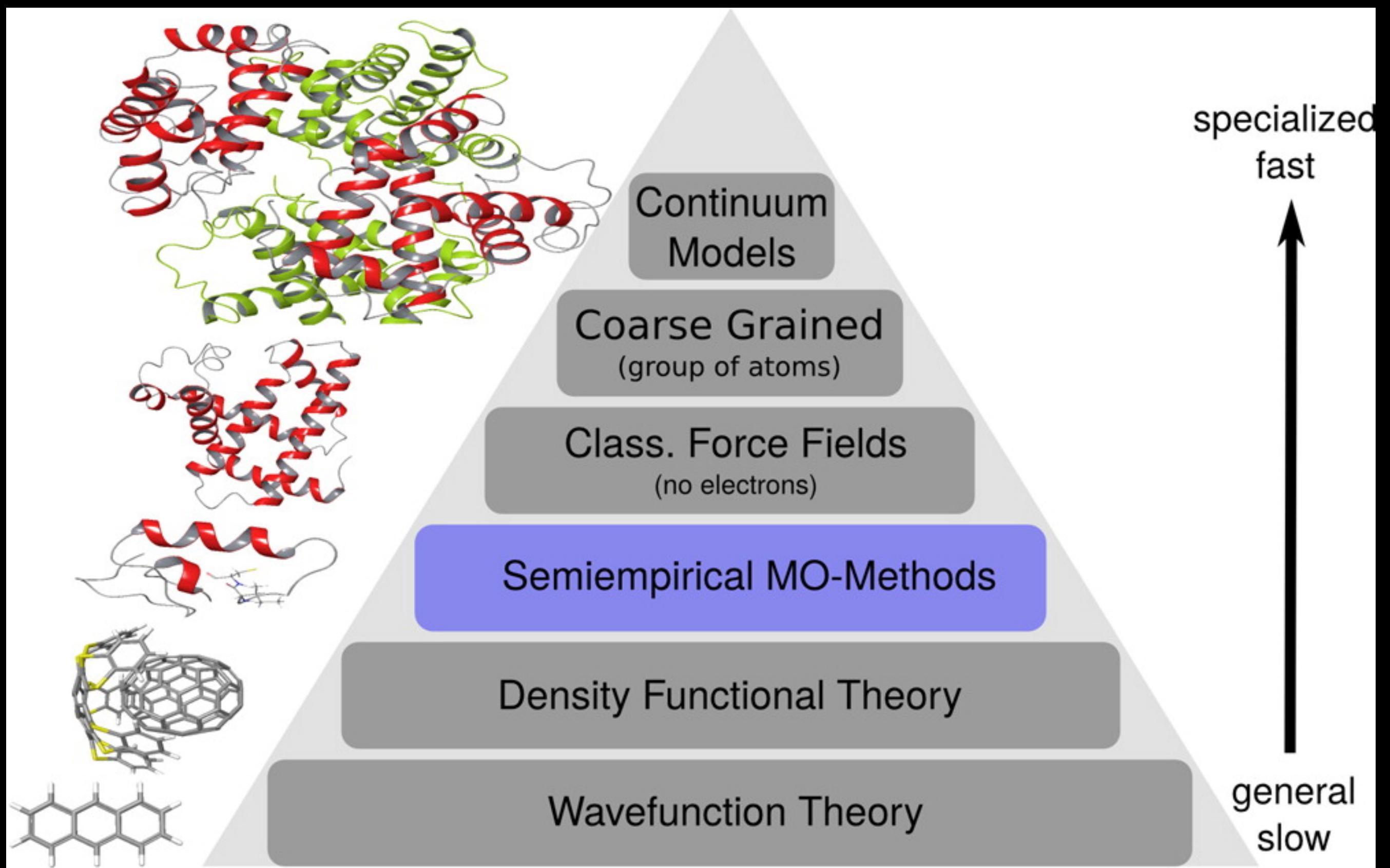
Consider the possible choices of S-D,  
this is called ***configuration interaction***  
(CI).  
Taking into the full account of choices is  
named full-CI.

# Correlation energy

$$E^{\text{corr}} \equiv E^{\text{real}} - E_0$$



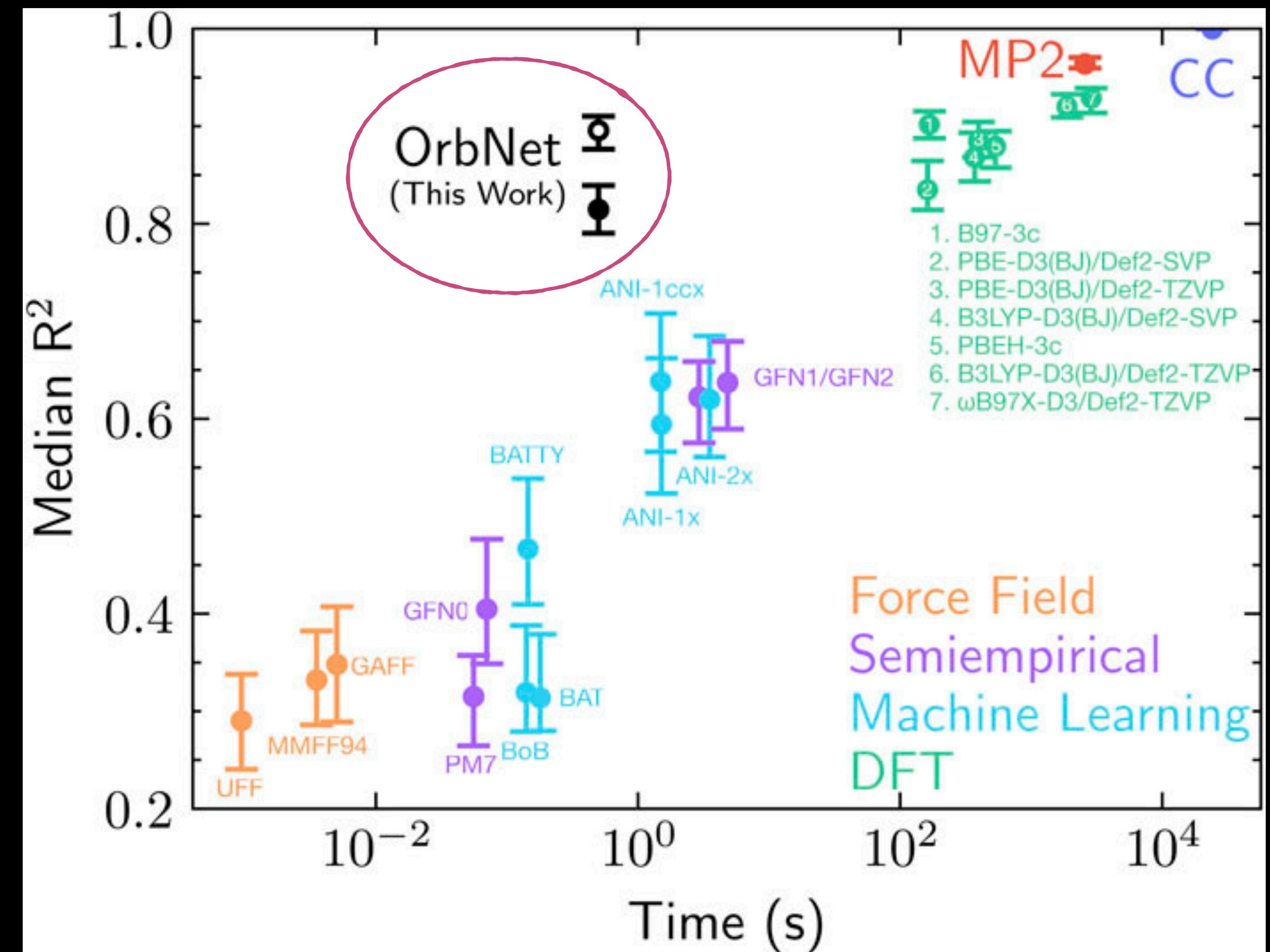
Energy from Hartree-Fock limit



S. Grimme et al. *J. Phys. Chem. Lett.* 2014, 5, 4275–4284

D. Folmsbee, G. Hutchison,  
*Int J Quantum Chem.* 2021;121:e26381.

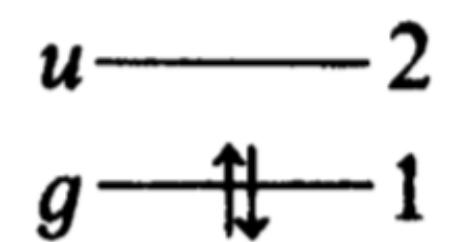
*J. Chem. Phys.* **2020**, *153*, 124111  
<https://doi.org/10.1063/5.0021955>



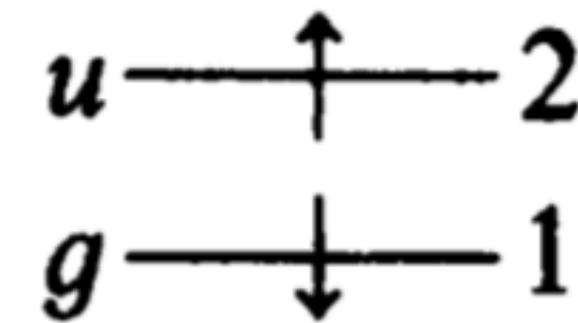
# Examples of S-Ds in minimal basis of H<sub>2</sub>

$$\binom{2*2}{2} = \frac{(4)!}{2!(2*2 - 2)!} = 6$$

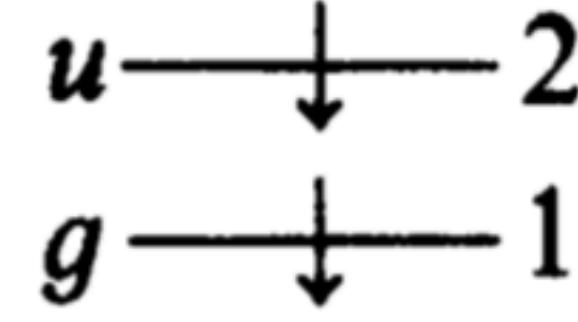
$$|\Psi_0\rangle = |\chi_1\chi_2\rangle = |\psi_1\bar{\psi}_1\rangle = |1\bar{1}\rangle$$



$$|\Psi_1^2\rangle = |2\bar{1}\rangle$$



$$|\Psi_1^2\rangle = |\bar{2}1\rangle$$



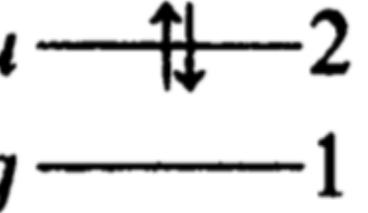
$$|\Psi_1^2\rangle = |12\rangle$$



$$|\Psi_1^2\rangle = |1\bar{2}\rangle$$



$$|\Psi_{1\bar{1}}^{2\bar{2}}\rangle = |2\bar{2}\rangle = |\chi_3\chi_4\rangle = |\Psi_{12}^{34}\rangle$$



$$|\Phi_0\rangle = c_0 |\Psi_0\rangle + c_{1\bar{1}}^{2\bar{2}} |\Psi_{1\bar{1}}^{2\bar{2}}\rangle = c_0 |\Psi_0\rangle + c_{12}^{34} |\Psi_{12}^{34}\rangle$$

# Operators and Matrix Elements

# From the minimal basis of H<sub>2</sub>

$$\hat{H} = \left( -\frac{1}{2} \nabla_1^2 - \frac{Z_A}{r_{1A}} - \frac{Z_B}{r_{1B}} \right) + \left( -\frac{1}{2} \nabla_2^2 - \frac{Z_A}{r_{2A}} - \frac{Z_B}{r_{1B}} \right) + \frac{1}{r_{12}}$$
$$= \boxed{\hat{h}(1) + \hat{h}(2)} + \frac{1}{r_{12}}$$

Core-Hamiltonian

One-body operator

$$\hat{\mathcal{O}}_1 = \hat{h}(1) + \hat{h}(2)$$

Two-body operator

$$\hat{\mathcal{O}}_2 = \frac{1}{r_{12}}$$

$$\langle \Psi_0 | \hat{h}(1) | \Psi_0 \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \left\{ 2^{-1/2} [\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)] \right\}^* \times$$

$$\hat{h}(\mathbf{r}_1) \left\{ 2^{-1/2} [\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)] \right\}$$

**Simplified**

**denotation:**

$$= \frac{1}{2} \int d\mathbf{x}_1 d\mathbf{x}_2 \left\{ \chi_1^* \chi_2^* \hat{h}(\mathbf{r}_1) \chi_1 \chi_2 + \chi_2^* \chi_1^* \hat{h}(\mathbf{r}_1) \chi_2 \chi_1 \right.$$

$$\chi_\alpha(\mathbf{x}_1) \chi_\beta(\mathbf{x}_2) \equiv \chi_\alpha \chi_\beta$$

$$\left. - \chi_1^* \chi_2^* \hat{h}(\mathbf{r}_1) \chi_2 \chi_1 - \chi_2^* \chi_1^* \hat{h}(\mathbf{r}_1) \chi_1 \chi_2 \right\}$$

$\int d\mathbf{x}_2 \chi_2^*(\mathbf{x}_2) \chi_1(\mathbf{x}_2) = 0$ 
  
 $\int d\mathbf{x}_2 \chi_1^*(\mathbf{x}_2) \chi_2(\mathbf{x}_2) = 0$

$$\langle \Psi_0 | \hat{h}(1) | \Psi_0 \rangle = \frac{1}{2} \langle 1 | \hat{h}(1) | 1 \rangle + \frac{1}{2} \langle 2 | \hat{h}(1) | 2 \rangle$$

One can prove:

$$\langle \Psi_0 | \hat{h}(2) | \Psi_0 \rangle = \langle \Psi_0 | \hat{h}(1) | \Psi_0 \rangle$$

$$\begin{aligned}\langle \Psi_0 | \hat{\mathcal{O}}_1 | \Psi_0 \rangle &= \langle 1 | \hat{h}(1) | 1 \rangle + \langle 2 | \hat{h}(1) | 2 \rangle \\ &= \langle 1 | \hat{h} | 1 \rangle + \langle 2 | \hat{h} | 2 \rangle\end{aligned}$$

One can also prove:

$$\langle \Psi_{12}^{34} | \hat{\mathcal{O}}_1 | \Psi_{12}^{34} \rangle = \langle 3 | \hat{h} | 3 \rangle + \langle 4 | \hat{h} | 4 \rangle$$

$$\langle \Psi_{12}^{34} | \hat{\mathcal{O}}_1 | \Psi_0 \rangle = 0$$

$$\begin{aligned}
\langle \Psi_0 | \hat{\mathcal{O}}_2 | \Psi_0 \rangle &= \frac{1}{2} \int d\mathbf{x}_1 d\mathbf{x}_2 \left\{ [\chi_1 \chi_2 - \chi_2 \chi_1]^* \frac{1}{r_{12}} [\chi_1 \chi_2 - \chi_2 \chi_1] \right\} \\
&= \frac{1}{2} \int d\mathbf{x}_1 d\mathbf{x}_2 \left\{ \chi_1^* \chi_2^* \frac{1}{r_{12}} \chi_1 \chi_2 + \chi_2^* \chi_1^* \frac{1}{r_{12}} \chi_2 \chi_1 \right. \\
&\quad \left. - \chi_1^* \chi_2^* \frac{1}{r_{12}} \chi_2 \chi_1 - \chi_2^* \chi_1^* \frac{1}{r_{12}} \chi_1 \chi_2 \right\}
\end{aligned}$$

Since  $r_{12} = r_{21}$

$$= \boxed{\int d\mathbf{x}_1 d\mathbf{x}_2 \chi_1^* \chi_2^* \frac{1}{r_{12}} \chi_1 \chi_2 - \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_1^* \chi_2^* \frac{1}{r_{12}} \chi_2 \chi_1}$$

**Two-electron integral**

# Notation of two-electron integrals

$$\langle ij | kl \rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle$$

$$= \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2)$$

$$\langle \Psi_0 | \hat{\mathcal{O}}_2 | \Psi_0 \rangle = \langle 12 | 12 \rangle - \langle 12 | 21 \rangle$$

# Some properties

$$\langle ij | kl \rangle = \langle ji | lk \rangle \quad \langle ij | kl \rangle = \langle kl | ij \rangle^*$$

Anti-symmetrized two-electron integral

$$\langle ij || kl \rangle = \langle ij | kl \rangle - \langle ij | lk \rangle$$

$$\langle ij || kk \rangle = \langle ij | kk \rangle - \langle ij | kk \rangle = 0$$

# Transition from spin orbital to spatial orbital

$$|\Psi_0\rangle = |\chi_1\chi_2\rangle = |\psi_1\bar{\psi}_1\rangle$$

$$E_0 = \langle \chi_1 | h | \chi_1 \rangle + \langle \chi_2 | h | \chi_2 \rangle + \langle \chi_1 \chi_2 | \chi_1 \chi_2 \rangle - \langle \chi_1 \chi_2 | \chi_2 \chi_1 \rangle$$

$$E_0 = \langle 1 | \hat{h} | 1 \rangle + \langle \bar{1} | \hat{h} | \bar{1} \rangle + \langle 1\bar{1} | 1\bar{1} \rangle - \langle 1\bar{1} | \bar{1}1 \rangle$$

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = \sum_a \langle a | h | a \rangle + \frac{1}{2} \sum_{ab} \langle ab || ab \rangle$$

Since  $\langle aa || aa \rangle = 0$ , and  $\langle ab || ab \rangle = \langle ba || ba \rangle$ , so:  $\sum_{a < b} \langle ab || ab \rangle = \frac{1}{2} \sum_{ab} \langle ab || ab \rangle$

$$\langle 1\bar{1} | 1\bar{1} \rangle = \int d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2 \psi_1^*(\mathbf{r}_1) \alpha^*(\omega_1) \psi_1^*(\mathbf{r}_1) \beta^*(\omega_1)$$

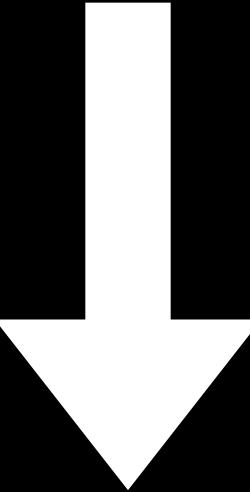
$$\begin{aligned} & \frac{1}{r_{12}} \psi_1(\mathbf{r}_1) \alpha(\omega_1) \psi_1(\mathbf{r}_2) \beta(\omega_2) \\ &= \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_1^*(\mathbf{r}_1) \psi_1^*(\mathbf{r}_1) \frac{1}{r_{12}} \psi_1(\mathbf{r}_1) \psi_1(\mathbf{r}_2) = (11 | 11) \end{aligned}$$

$$\langle 1\bar{1} | \bar{1}1 \rangle = \int d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2 \psi_1^*(\mathbf{r}_1) \alpha^*(\omega_1) \psi_1^*(\mathbf{r}_1) \beta^*(\omega_1)$$

$$\begin{aligned} & \frac{1}{r_{12}} \psi_1(\mathbf{r}_1) \beta(\omega_1) \psi_1(\mathbf{r}_2) \alpha(\omega_2) = 0 \end{aligned}$$

$$\langle ik | jl \rangle = (ij | kl)$$

$$\begin{aligned} E_0 &= 2(\psi_1 | \hat{h} | \psi_1) + (\psi_1 \psi_1 | \psi_1 \psi_1) \\ &= 2(1 | \hat{h} | 1) + (11 | 11) \end{aligned}$$



$$E_0 = 2 \sum_a^{N/2} (a | h | a) + \sum_a^{N/2} \sum_b^{N/2} [2(aa | bb) - (ab | ba)]$$

# Coulomb integral and Exchange integral

$$J_{ij} = (ii | jj) = \langle ij | ij \rangle$$

$$K_{ij} = (ij | ji) = \langle ij | ji \rangle$$

# Hartree-Fock equation

# Collection of what we have

$$|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_N\rangle$$

$$\chi_i(\vec{r}) = \sigma_i(\omega) \sum_{\alpha=1}^N c_{i\alpha} \phi_\alpha(\vec{r})$$

$$\langle a | h | a \rangle = \int \psi_a^*(\vec{r}) \left( -\frac{1}{2} \nabla^2 - \sum_{A=1}^M \frac{Z_A}{r_{a,A}} \right) \psi_a(\vec{r}) d^3r \langle \sigma_a | \sigma_a \rangle$$

$$\begin{aligned} \langle ab | | ab \rangle = & \int \int \psi_a^*(\vec{r}_1) \psi_b^* \left[ (\vec{r}_2) \frac{1}{r_{12}} \psi_a(\vec{r}_1) \psi_b(\vec{r}_2) \langle \sigma_a | \sigma_a \rangle \langle \sigma_b | \sigma_b \rangle - \right. \\ & \left. \psi_b(\vec{r}_1) \psi_a(\vec{r}_2) \langle \sigma_a | \sigma_b \rangle \langle \sigma_b | \sigma_a \rangle \right] d^3r_1 d^3r_2 \end{aligned}$$

$$\chi_i(\vec{r}) = \sigma_i(\omega) \sum_{\alpha=1}^N c_{i\alpha} \phi_{\alpha}(\vec{r})$$

Example (fixed coefficients):

$$\psi_1 = [2(1 + S)]^{-1/2}(\phi_1 + \phi_2) \quad S = \langle \phi_1 | \phi_2 \rangle \quad \chi_1 = \psi_1(\mathbf{r})\alpha(\omega)$$

$$\psi_2 = [2(1 + S)]^{-1/2}(\phi_1 - \phi_2) \quad \chi_2 = \psi_1(\mathbf{r})\beta(\omega)$$

$$\phi_1(\vec{r}) = \frac{1}{\sqrt{\pi}} e^{-|\vec{r} - \vec{R}_1|} \quad \chi_3 = \psi_2(\mathbf{r})\alpha(\omega)$$

$$\phi_2(\vec{r}) = \frac{1}{\sqrt{\pi}} e^{-|\vec{r} - \vec{R}_2|} \quad \chi_4 = \psi_2(\mathbf{r})\beta(\omega)$$

# Matrix elements

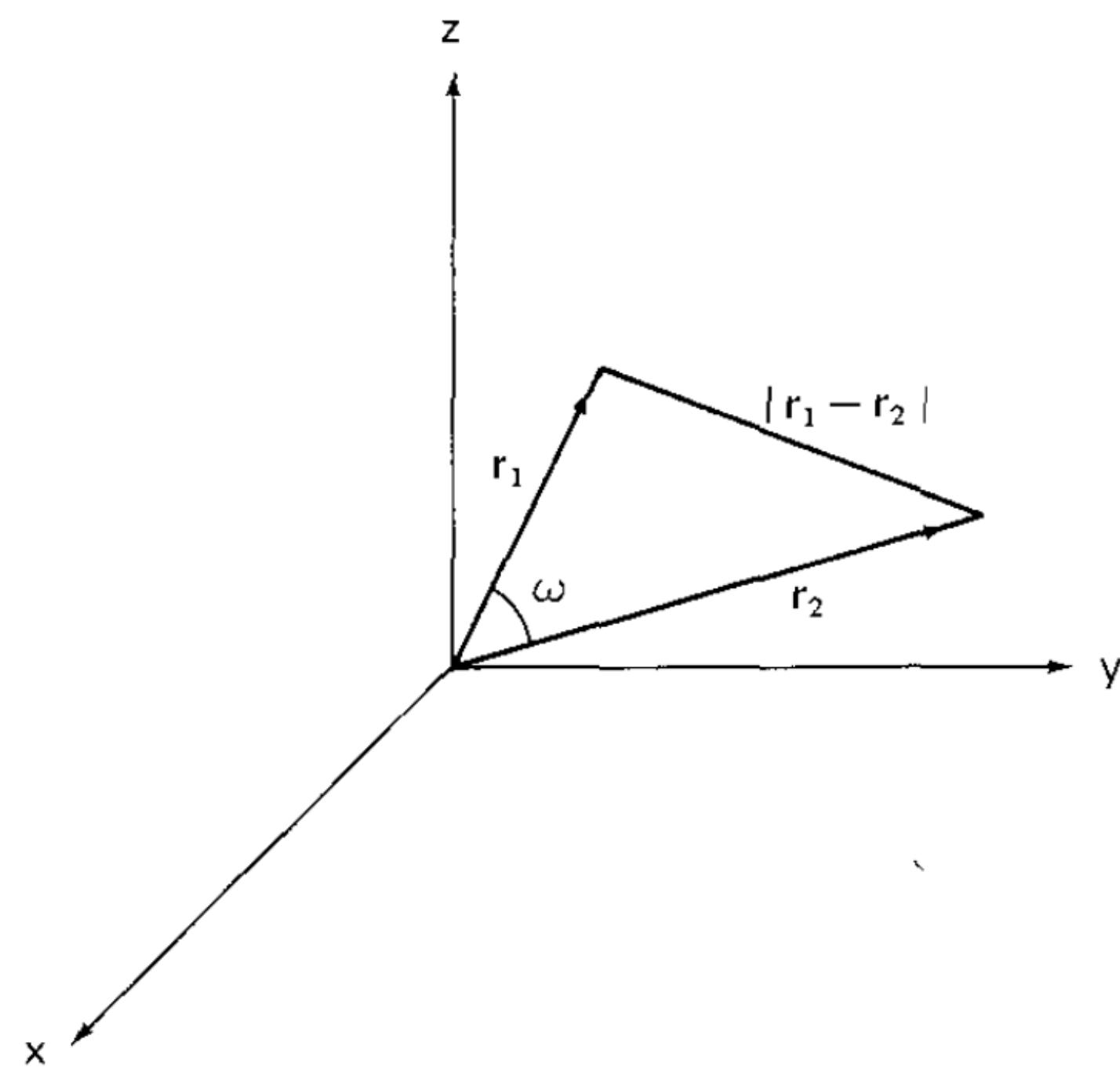


FIG. 1.3 Notation and coordinate system for Eq. (1.2-20).

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} P_l(\cos \omega)$$

In which  $r_<$  stands for the smaller of the two distances  $|\vec{r}_1|$  and  $|\vec{r}_2|$ ,  $r_>$  is the greater of the two distances, and  $P_l(\cos \omega)$  is a Legendre polynomial.

Since  $\vec{r}_1 = (r_1, \theta_1, \varphi_1)$  and  $\vec{r}_2 = (r_2, \theta_2, \varphi_2)$ , then the angle  $\omega$  is the angle between the two directions. The addition theorem:

$$P_l(\cos \omega) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_{lm}^*(\theta_1, \varphi_1) Y_{lm}(\theta_2, \varphi_2)$$

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_{lm}^*(\theta_1, \varphi_1) Y_{lm}(\theta_2, \varphi_2)$$

# Distraction: Lagrange multiplier

A cylinder, with its radius  $r$  and height  $h$ , given its surface known as  $6\pi$ , what's its largest volume?

$$V = \pi r^2 h \quad S = 2\pi r h + 2\pi r^2 = 6\pi$$

$$\mathcal{L} = V - \lambda(S - 6\pi) = \pi r^2 h - \lambda(2\pi r h + 2\pi r^2 - 6\pi)$$



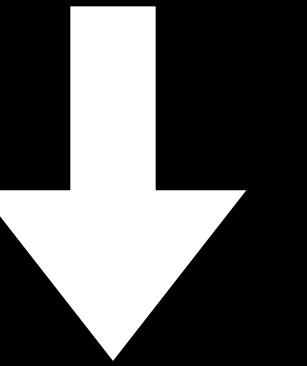
$$\frac{\partial \mathcal{L}}{\partial r} = 2\pi r h - \lambda(2\pi h + 4\pi r) = 0 \quad rh - \lambda h - 2\lambda r = 0$$

$$\frac{\partial \mathcal{L}}{\partial h} = \pi r^2 - \lambda(2\pi r) = 0 \quad r = 2\lambda \quad h = 4\lambda \quad \lambda = \frac{1}{2} \quad \begin{cases} h = 2 \\ r = 1 \end{cases}$$

$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_N\rangle \quad E_0 = \langle\Psi_0|\hat{H}|\Psi_0\rangle = \sum_a \langle a|h|a\rangle + \frac{1}{2} \sum_{ab} \langle ab||ab\rangle$$

$$\langle a|b\rangle=\delta_{ab}$$

$$\mathcal{L} = E_0[\{\chi_a\}] - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} (\langle a|b\rangle - \delta_{ab})$$



$$\delta\mathcal{L} = \delta E_0[\{\chi_a\}] - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} \delta\langle a|b\rangle = 0$$

$$\delta\langle a | b \rangle = \langle \delta a | b \rangle + \langle a | \delta b \rangle = \langle \delta a | b \rangle + c.c.$$

$$\begin{aligned} \delta E_0 &= \sum_{a=1}^N [\langle \delta a | h | a \rangle + \langle a | h | \delta a \rangle] & \langle \delta a | h | a \rangle = \langle a | h | \delta a \rangle^* \\ &+ \frac{1}{2} \sum_{a,b} [ \langle (\delta a)b | ab \rangle + \langle a(\delta b) | ab \rangle + \langle ab | (\delta a)b \rangle + \langle ab | a(\delta b) \rangle ] \\ &- \frac{1}{2} \sum_{a,b} [ \langle (\delta a)b | ba \rangle + \langle a(\delta b) | ba \rangle + \langle ab | (\delta b)a \rangle + \langle ab | b(\delta a) \rangle ] \end{aligned}$$

$$\begin{aligned} \langle ij | kl \rangle &= \langle ji | lk \rangle \\ \Rightarrow \langle a(\delta b) | ab \rangle &= \langle (\delta b)a | ba \rangle \end{aligned}$$

$$\begin{aligned} \sum_{ab} \langle (\delta b)a | ba \rangle &= \sum_{ba} \langle (\delta a)b | ab \rangle \\ &= \sum_{ab} \langle (\delta a)b | ab \rangle \end{aligned}$$

$$\delta E_0 = \sum_{a=1}^N \langle \delta a | h | a \rangle + \sum_{a,b} \langle (\delta a)b | ab \rangle - \sum_{a,b} \langle (\delta a)b | ba \rangle \\ + c.c.$$

$$\delta \mathcal{L} = \sum_{a=1}^N \langle \delta a | h | a \rangle + \sum_{a,b} [\langle (\delta a)b | ab \rangle - \langle (\delta a)b | ba \rangle] \\ - \sum_{ab} \epsilon_{ab} \langle \delta a | b \rangle + c.c. = 0 \\ = \sum_{a=1}^N \left\{ \langle \delta a | h | a \rangle + \sum_{b=1}^N [\langle (\delta a)b | ab \rangle - \langle (\delta a)b | ba \rangle] \right. \\ \left. - \sum_{b=1}^N \epsilon_{ab} \langle \delta a | b \rangle \right\} + c.c. = 0$$

$$\delta \mathcal{L} = \sum_{a=1}^N \int \mathrm{d}\boldsymbol{x}_1 (\delta \chi_a^*) \left\{ \hat{h} \chi_a + \sum_{b=1}^N \left[ \hat{\mathcal{J}}_b - \hat{\mathcal{K}}_b \right] \chi_a - \sum_{b=1}^N \varepsilon_{ab} \chi_b \right\} + c.c.=0$$

$$\hat{h} \chi_a + \sum_{b=1}^N \left[ \hat{\mathcal{J}}_b - \hat{\mathcal{K}}_b \right] \chi_a = \sum_{b=1}^N \varepsilon_{ab} \chi_b$$

$$\hat{\mathcal{J}}_b \chi_a = \hat{\mathcal{J}}_b(1) \chi_a(1) = \left[ \int \mathrm{d}\boldsymbol{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_b(2) \right] \chi_a(1)$$

$$\hat{\mathcal{K}}_b \chi_a = \hat{\mathcal{K}}_b(1) \chi_a(1) = \left[ \int \mathrm{d}\boldsymbol{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_a(2) \right] \chi_b(1)$$

$$\hat{h}\chi_a + \sum_{b=1}^N [\hat{\mathcal{J}}_b - \hat{\mathcal{K}}_b] \chi_a = \sum_{b=1}^N \varepsilon_{ab} \chi_b$$

Fock operator:

$$\hat{\mathcal{F}} = \hat{h} + \sum_{b=1}^N [\hat{\mathcal{J}}_b - \hat{\mathcal{K}}_b]$$

Hartree-Fock  
equation:

$$\hat{\mathcal{F}}\chi_a = \sum_{b=1}^N \varepsilon_{ab} \chi_b$$

# Canonical H-F equation

$$\chi'_a = \sum_b \chi_b U_{ba} \quad |\Psi'_0\rangle = \det(\mathbf{U}) |\Psi_0\rangle$$

$$\mathbf{U}^\dagger \mathbf{U} = 1 \quad \det [\mathbf{U}^\dagger \mathbf{U}] = |\det(\mathbf{U})|^2 = 1 \quad \det(\mathbf{U}) = e^{i\phi} \quad (\pm 1)$$

$$\sum_a \hat{\mathcal{J}}'_a(1) = \sum_a \int d\mathbf{x}_2 \chi_b'^*(2) r_{12}^{-1} \chi_b'(2) \sum_a U_{ba}^* U_{ca} = (\mathbf{U} \mathbf{U}^\dagger)_{cb} = \delta_{cb}$$

$$= \sum_{bc} \left[ \sum_a U_{ba}^* U_{ca} \right] \int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_b(2) = \boxed{\sum_a \hat{\mathcal{J}}_a(1)}$$

$$\hat{\mathcal{F}}'=\hat{\mathcal{F}}$$

$$\varepsilon' = \mathbf{U}^\dagger\varepsilon\mathbf{U}$$

$$(\partial_{\mu}^{\alpha} \phi) (\partial_{\mu}^{\beta} \phi) = \delta^{\alpha \beta} \phi^2 + \text{higher order terms}$$

$$\langle \psi_1 | \psi_2 \rangle = \int d^3x \psi_1^*(x) \psi_2(x)$$

$$\hat{\mathcal{F}}\left|\chi_a^{'}\right\rangle =\varepsilon _a^{'}\left|\chi_a^{'}\right\rangle$$

$$\mathcal{L}_\mathrm{D} = \frac{1}{2}\sum_{i=1}^N\sum_{j=1}^N\sum_{k=1}^N\sum_{l=1}^N\delta_{ijkl}\left(\frac{\partial}{\partial x_i}\phi_j\right)\left(\frac{\partial}{\partial x_k}\phi_l\right)$$

$$\mathcal{L}_{\rm D} = \frac{1}{2}\sum_{i=1}^N\sum_{j=1}^N\sum_{k=1}^N\sum_{l=1}^N\delta_{ijkl}\left(\frac{\partial}{\partial x_i}\phi_j\right)\left(\frac{\partial}{\partial x_k}\phi_l\right)$$

$$\mathcal{L}_\mathrm{D} = \frac{1}{2}\sum_{i=1}^N\sum_{j=1}^N\sum_{k=1}^N\sum_{l=1}^N\delta_{ijkl}\left(\frac{\partial}{\partial x_i}\phi_j\right)\left(\frac{\partial}{\partial x_k}\phi_l\right)$$

$$\mathcal{L}_{\rm D} = \frac{1}{2}\sum_{i=1}^N\sum_{j=1}^N\sum_{k=1}^N\sum_{l=1}^N\delta_{ijkl}\left(\frac{\partial}{\partial x_i}\phi_j\right)\left(\frac{\partial}{\partial x_k}\phi_l\right)$$

$$\mathcal{L}_\mathrm{D} = \frac{1}{2}\sum_{i=1}^N\sum_{j=1}^N\sum_{k=1}^N\sum_{l=1}^N\delta_{ijkl}\left(\frac{\partial}{\partial x_i}\phi_j\right)\left(\frac{\partial}{\partial x_k}\phi_l\right)$$

End